THE

PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED BY THE

AMERICAN PHYSICAL SOCIETY

EDITORS

Second Series *April, 1929* *Vol. 33, No. 4*

THE

PHYSICAL REVIEW

TOTAL REFLECTION OF X-RAYS FROM NICKEL FILMS PART II

By Hiram W. Edwards

Abstract

Variation of critical angle with thickness of film for films deposited on platinum. —The total reflection of x-rays ($\lambda = 0.707$A) is obtained from a series of thin nickel films of thickness varying from zero to 2.05×10^{-6} cm. The films were sputtered upon thick platinum which was, in turn, sputtered upon a glass support. The critical angle for each film was measured. The values of the critical angle varied from 0.0040 radians (that of the bare platinum) to 0.0034 radians. With the exception of an increase in the critical angle (maximum value of 0.0043 radians) for the thinnest films, the critical angle decreased logarithmically with increasing thickness of the nickel film. The value obtained from the thickest film agrees with that calculated by the Lorentz dispersion formula. These results, together with those reported earlier seem to prove conclusively that the phenomenon of total reflection is not a purely surface phenomenon but is one which requires a layer of metal of probably definite thickness for the particular reflecting matter and wave-length of radiation used. An explanation for the variation of the critical angle with the thickness of the nickel films is given. This is based upon the assumption that the contribution to the intensity of the reflected ray made by the deepest electrons will be effective only when the total length of the path of the radiation in the metal is not too great. The maximum effective depth is that which reduces the intensity of the emerging radiation by absorption to a value less than that which may be detected in the reflected beam.

IN A previous report[1] the writer presented the results of an experimental determination of the critical angle of several thin nickel films sputtered upon glass supports. The results of that investigation gave values of the critical angles, for $\lambda = 0.707$A, varying from a minimum value of 0.0016 radians, that of the unsputtered glass, to a maximum value of 0.0034 radians. The final value agreed with that calculated by the Lorentz dispersion formula, assuming a density of 8.75 gm/cc for nickel. The increasing value of the critical angle with increasing thickness of the nickel was taken as evidence for supposing that the electrons of the underlying glass support participated in the phenomenon of reflection and gave values for the critical angles which might have been construed as due to abnormally small values of the density of the nickel.

[1] Edwards, Phys. Rev. **32**, 712 (1928).

In order to obtain conclusive evidence to test this hypothesis, a second series of nickel films was prepared. The thicknesses increased from zero to a final value of about 2.05×10^{-5} cm. In this test, however, the nickel was sputtered upon thick platinum films. Eight platinum films were made by sputtering platinum upon flat pieces of glass. All the glass supports were cut from a single piece of glass and each received the same amount of platinum. Each platinum film was sputtered for 30 minutes under as nearly identical conditions of sputtering current, voltage, gas pressure, and cathode receiving-surface distance, as was possible to maintain. The thickness of the platinum was not measured but was thick enough to make the film entirely opaque to intense sources of light and to give the same value of the critical angle by x-ray measurements as was obtained from a film fully three times as thick.

The nickel films were sputtered upon the platinum mirrors under similar sputtering conditions except that the time of sputtering for the seven films varied from 2 to 50 minutes.

The critical angles were obtained by the method and with the apparatus described previously.[2] The results are probably accurate to one or two percent of the given values. The $K\alpha$ lines from a molybdenum water-cooled tube served as a source of x-radiation.

The thicknesses of the films were calculated from the time of sputtering, from the results obtained by weighing the film deposited upon another piece of glass sputtered for 30 minutes as a basis for the calculations. The thickness of this film was found to be 1.23×10^{-5} cm. The results of the measurements are tabulated as follows:

TABLE I. *Variations of critical angle with thickness of nickel films.*

Mirror No.	Time of sputtering (min.)	Critical angle (radians)	Color of film	Thickness ($cm\times10^{5}$)
1	0	0.0040	white	0.0
2	2	0.0043	white	0.08
3	3	0.0043	light yellow	0.12
4	4	0.0043	yellow orange	0.16
5	5	0.0041	purple	0.205
6	6	0.0039	blue	0.25
7	10	0.0037	white	0.41
8	50	0.0034	white	2.05
	Value calculated from dispersion theory	0.0034		—

In order to show the manner in which the critical angle varies with the thickness of the nickel film (expressed in terms of sputtering time) the above results have been plotted together with the previous results obtained by sputtering the nickel films directly upon glass without the intervening film of platinum.

[2] Edwards, Phys. Rev. **30**, 91 (1927).

An inspection of the plotted values of the critical angle shows that the proper thickness of the film necessary to give the correct value of the critical angle is approached logarithmically. It is to be inferred from the character of the two curves that any theory which might be proposed to explain this phenomenon would probably indicate that an infinite thickness of the reflecting material would be necessary in order to obtain a correct value of the critical angle. Within the ordinary limits of error in measurement, this limiting value of the necessary thickness would, as the evidence presented shows, be reached very much sooner.

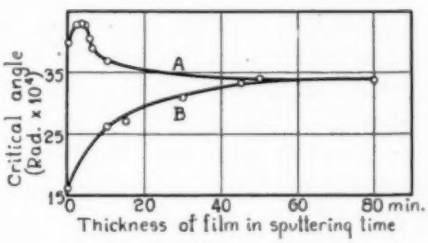

Fig. 1. Experimental curves showing the dependence of the critical angle of nickel films upon the thickness of the film and the underlying material. Curve *A*, nickel over platinum. Curve *B*, nickel over glass.

The above experimental results permit of a rather simple theoretical explanation. If we assume that the path of the x-radiation in the reflecting substance is along the line of the incident beam, since the index of refraction is very nearly equal to one, and that the scattered radiation is in line with the reflected ray, then we may determine the total length of the path in the metal traversed by the radiation from any underlying electrons. The intensity of the radiation from any scattering electron, as it emerges from the reflecting surface, will depend upon the intensity of the incident beam, the absorption coefficient of the reflecting material and the length of the path traversed in the metal. If an electron is to contribute any measurable intensity to the reflected ray and therefore participate in the phenomenon of reflection, it must not lie too deeply in the metal.

If the distance of a contributing electron below the reflecting surface is indicated by the symbol d and the critical angle (in radians) is called c, then the length, x, of the path in the reflecting medium which the radiation must traverse is given by $x=2d/c$. The intensity of the emerging radiation will be expressed by the relation

$$I=I_0e^{-\mu_m\rho x}$$

where the symbols have their usual meaning. With these two equations we may therefore determine the necessary thickness of a film in order to have the contribution by the deepest electrons too small to affect the intensity of the reflected ray. If the critical angle may be made with a measurement that has an error of 1 percent, then the intensity of the radiation from the deepest electrons should be less than 1 percent of the intensity of the incident beam. We could therefore assign a value of 100 to the ratio I_0/I.

We may apply this explanation to the experimental data given above. The values of the measured critical angles are probably accurate to better than a 1 percent error. Putting $I_0/I=100$ and taking the mass coefficient

of absorption of nickel at 48.2 for the radiation used, and $\rho = 8.75$ gm/cc, the calculated value of x is found to be 0.011 cm. The correct value of the critical angle for nickel when using the $K\alpha$ radiation from molybdenum is probably 0.0034 radians. From these values d comes out to be equal to 1.87×10^{-6} cm, which is in close agreement with 2.05×10^{-5} cm, the thickness of the nickel film on platinum which gave a correct measured value of the critical angle.

Attention should be called to one other result in the measurements of the critical angle obtained from the four thinnest nickel films on platinum. Each of these gave a value which was greater than that of the bare platinum. These results would seem to indicate that the electronic density of the combined metals is greater than that of either the nickel or platinum alone. If this is the case one would expect that the first nickel atoms deposited upon the platinum are embedded among the platinum atoms producing an alloy having a greater density than the platinum alone. The fact that the nickel films adhere tenaciously to the platinum films supports this viewpoint.

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January 15, 1929.

ON σ-TYPE DOUBLING AND ELECTRON SPIN IN THE SPECTRA OF DIATOMIC MOLECULES

By J. H. Van Vleck

Abstract

1. The distortion due to molecular rotation causes the width of a spin multiplet to depend on j, and tends to uncouple the spin axis from quantization relative to the axis of figure, thus bringing about a gradual passage from Hund's case (a) to (b). Another rotational effect is the "sigma-type doubling" of spectral lines due to removal of the degeneracy associated with the equality in energy of left- and right-handed axial rotations in stationary molecules. The present paper treats these two effects, especially their interrelation.

2. As a needed mathematical preliminary we calculate the *perturbing matrix elements* due to the components of angular momentum perpendicular to the figure axis, which are neglected in the usual treatment of the rotating molecule as a symmetrical top. This calculation would be similar to Kronig's and Wigner and Witmer's were it not for inclusion of the spin. This is handled by Pauli's scheme of two wave functions per electron, especially his method of transforming them from one Cartesian system to another by the Cayley-Klein parameters. The results also hold with Dirac's "quantum theory of the electron," as Dirac's quartet of wave functions transform under a rotation like two independent Pauli pairs. Although the orbital and spin angular momentum operators look superficially different, it is shown that their gyroscopic effects enter additively as commonly supposed, and that in the first approximation the effect of the spin is to make the rotational energy (except for an additive constant) that of the symmetrical top with $\sigma_1+\sigma_s$ in place of σ_1.

3. Neglect of the relatively small sigma-doubling yields identically the formulas for the *rotational distortion of spin multiplets* which Hill and Van Vleck obtained by a different, alternative method that used Hund's case (b) rather than (a) as the unperturbed system.

4. *Singlet P states* should exhibit a sigma doubling proportional to $j(j+1)$ and D states ordinarily a negligible doubling. Our technique of calculation differs slightly from that of Kronig, who obtained a similar result for singlet spectra (as did Hill and V. V. with a simple model), in that the degeneracy is removed in the final rather than in the initial approximation.

5. In ^2P *states* the spin profoundly modifies the sigma doubling. In case (b) both spin components should exhibit equal doublings proportional to $j_k(j_k+1)$, but in case (a) the $P_{3/2}$ sigma doubling should be negligible, but the $P_{1/2}$ fairly large and proportional to $j+1/2$. Formulas are developed for the sigma-doublet width which apply throughout the range between (a) and (b). The pronounced doubling of the $P_{1/2}$ component in case (a) is due to a rather complicated superposition of the rotational distortion on the magnetic coupling between the components of spin and orbital angular momentum which are perpendicular to the axis of figure.

6. ^2S *states*. A similar superposition explains the so-called "rho-type doubling" in ^2S states whereby levels of like j_k but unlike j differ by small amounts proportional to $j_k+1/2$. This explanation differs from the usual interpretation of this doubling as due to magnetic moment developed by orbital motions, and seems to give a slightly larger effect.

7. ^3P *states*. In case (b) all three components should have equal doublings proportional to $j_k(j_k+1)$ but in (a) the P_0 and P_1 doublings should be respectively independent of j and proportional to $j(j+1)$, while the P_2 is negligible. The large

splitting of the P_0 component, whose exceptional behavior is due to its having $\sigma=0$, is due largely to magnetic action effective even in a stationary molecule, and so has a different origin than the usual sigma doubling due to rotational distortion.

8. *A summary and comparison with experimental data* taken from Mulliken's following paper are finally given. There is a striking agreement between theory and experiment on the type of variation with j in the various cases, especially the asymmetrical behavior of the various multiplet components in case (a). The theoretical orders of absolute magnitude are also confirmed, as evidenced by the reasonable values of the frequencies which must be assumed to give the observed separations.

I. Introduction[1]

STATIONARY MOLECULES. To calculate the electronic, though not of course the rotational and vibrational, levels of a diatomic molecule one can, to a first approximation suppose the nuclei at rest. This has been shown by Born and Oppenheimer.[2] Such a fictitious molecule with fixed nuclei we term stationary. Its "parallel" components of orbital and of spin angular momentum ordinarily have quantized values σ_l and σ_s. We throughout measure angular momentum in multiples of the quantum unit $h/2\pi$, and also for brevity we always speak of the "parallel" or "perpendicular" component when more explicitly we mean the component which is parallel or perpendicular to the axis of figure connecting the nuclei. (Unless otherwise stated, it is supposed that the nuclei are far enough apart so that the resultant field which they together exert on the electrons departs appreciably from central character. If this "non-centralness," as we shall call it, were not large compared to the magnetic interaction, only the sum $\sigma=\sigma_l+\sigma_s$, rather than σ_l and σ_s individually, would be quantized.) Two features of stationary molecules which are of particular importance for the present paper are the following: (1) with given σ_l different values of the quantum number σ_s generate a "spin multiplet," which arises from the so-called magnetic interaction between the spin and orbital angular momenta. (2) The energy is invariant if the signs of both σ_l and σ_s are simultaneously reversed, which merely converts a left into a right-handed rotation about the axis of figure, or vica versa. The energy levels $+\sigma_l, +\sigma_s$ and $-\sigma_l, -\sigma_s$ are thus a degenerate pair.

Rotating molecules. Besides introducing primarily the familiar rotational and vibrational energies, the motion of the nuclei modifies the effects (1) and (2), as first suggested by Hund.[3] The study of these modifications is the purpose of this paper. As regards (1), the energy due to magnetic interaction is no longer the same as in a stationary molecule, but depends on the amount of rotation j. This is the phenomenon of the rotational distortion of spin multiplets, which was treated in the old quantum theory by Kemble.[4] If this distortion is large, the parallel component of spin angular momentum

[1] A preliminary account of the present paper was given in abstract 36 of the June 1928 program of the American Physical Society (Phys. Rev. **32**, 327, 1928).

[2] Born and Oppenheimer, Ann. der Physik **84**, 457 (1927).

[3] F. Hund, Zeits. f. Physik **36**, 657 (1926); **42**, 93 (1927).

[4] E. C. Kemble, Phys. Rev. **30**, 387 (1927).

no longer has a quantized value σ_s. Instead in the limit of negligibly weak magnetic interaction compared to rotation, which is Hund's case (b), the orbital electronic angular momentum is compounded with that due to nuclear motion to form a resultant j_k, and then j_k and s are compounded to form a resultant j. The other limiting case of relatively strong magnetic interaction, where the parallel component of s is quantized, constitutes Hund's case (a). (See diagrams, p. 253 of ref. 5). As regards (2), it is found that the degeneracy associated with the pair of states $+\sigma_l$, $+\sigma_s$ and $-\sigma_l$, $-\sigma_s$ is removed by the rotation. The attendant separation of otherwise coincident energy levels and splitting up of spectral lines constitutes in Mulliken's terminology the phenomenon of "sigma-type doubling," and is not to be confused with the much coarser spin doubling found in molecules having $s=1/2$.

Previous work. After Kemble's[4] ingenious pioneer work in the old quantum theory, Hill and Van Vleck[5] calculated formulas for the rotational distortion of spin multiplets in the new quantum mechanics, using Hund's case (b) as the unperturbed system. Their paper will be referred to as "Hill and V. V." Its last section gave an elementary treatment of sigma-type doubling in singlet spectra, using Hund's case (d) as the initial system. By (d) is meant that the non-centralness is so small compared to rotational distortion that not even the parallel component of orbital angular momentum is quantized. The present paper uses (a) rather than (b) or (d) as the original system from which perturbations are figured. In the problem of multiplet distortion this use of (a) simply furnishes an alternative and about equally good method to that of Hill and V. V., but in the treatment of sigma-doubling it permits a much more accurate representation of the details of the molecular dynamics than did the over-simplified though very convenient model used in Hill and V. V.'s last section. The theory of sigma-type doubling in singlet spectra has also been discussed in two papers by Kronig,[6] and has also been studied by Wigner and Witmer.[7] Kronig's first paper, which was previous to Hill and V. V., demonstrated the possibility of sigma-doubling and developed selection rules, previously formulated empirically by Hulthén,[8] which govern the combinations of the various types of levels. Kronig's second article calculated the magnitude of the frequency separation of the

[5] E. Hill and J. H. Van Vleck, Phys. Rev. **32,** 250 (1928). This paper used the notation σ_k, k instead of the present σ_l, l. Their choice of arbitrary phases is different from ours and would require insertion of a minus sign in our Eq. (31). With our choice the two elements of the transformation matrix T given in their Eq. (38) would be reversed in sign.

[6] R. de L. Kronig, Zeits. f. Physik, **46,** 814; **50,** 347 (1928). Unless otherwise stated, all references to Kronig's equations, etc., are to his second rather than first paper, and by Kronig symmetry or antisymmetry we mean even or oddness under his transformation (15). The writer is indebted to Professor Kronig for the opportunity of seeing his second manuscript in advance of publication.

[7] E. Wigner and E. E. Witmer, Zeits. f. Physik **51,** 859 (1928), especially footnote, p. 860. To avoid duplication with Kronig they do not publish the details of their calculation of the sigma doubling.

[8] E. Hulthén, Zeits. f. Physik **46,** 349 (1927); also R. S. Mulliken, Phys. Rev. **28,** 1202 (1926).

sigma-doubling components, and also gave a more accurate formulation and more elegant proof of the selection principles than in his first paper. The present article will not attempt to treat these selection rules, but only the doublet widths, as the combining properties of the terms are nicely covered in Kronig's papers, as well as analysed for a simple model by Hill and V. V. The previous work shows that it is indeed possible to divide the levels into two classes x and y (Kronig's "even" and "uneven" terms) such that the only possible transitions are those connecting an x and a y state, so that two x or two y states never combine in the absence of external fields. One sigma-doublet component is, of course, of the x-type and the other of the y, the component of higher energy being alternately x and y as j progressively increases by unity. We show in footnote 9 that the extension of the selection principles to include the electron spin occasions no difficulty.

- Kronig's papers did not consider the electron spin, nor did the part of Hill and V. V. on sigma doubling, and an essential feature of the present article is that it treats the theory of sigma-doubling inclusive of spin. This is an important increase in generality, for some of the most striking sigma-doubling phenomena are found in other than singlet spectra, and are influenced by the spin in a very interesting way.

The following section 2 of the present paper is primarily mathematical in character and is fairly distinct in content from the remainder. It consists of the calculation of the matrix elements which are neglected in treating a molecule in Hund's case (a) as a symmetrical top, and which are responsible for both the rotational distortion and sigma-doubling phenomena. To a considerable extent this calculation parallels Kronig's though made independently. It, however, includes the spin, and gives some details, such as are involved in passing from our Eq. (10) to (29), which Kronig omits, but which do not seem trivial. Although the final result (29) of section 2 is vital to later sections, we have tried to make these fairly readable without a thorough perusal of section 2.

Quantum number notation. Our nomenclature is in the main the same as in Mulliken's well known series of papers. The recent Hund-Wigner-Witmer scheme appeared too late to be feasible. The numbers σ_l, σ_s and $\sigma(=\sigma_l+\sigma_s)$

[9] Although Kronig did not consider the spin, the invariance of the wave equation under a "reflection" such as is embodied in his Eq. (15) and from which he derives the selection rules, still holds even when the Pauli or Dirac spin operators are included. For it is readily seen that the transformation $x=x$, $y=-y$, $z=z$, which is our system of coordinates is equivalent to the ξ, η, ζ, ϕ, part of Kronig's transformation (15) demands the reversal of the sign of the operators s_x, s_z but not s_y, just as it does the reversal of the orbital angular momentum operators $l_x=i^{-1}(y\partial\cdot\cdot/\partial z-z\partial\cdot\cdot/\partial y)$ and l_z but not l_y. Further our Eqs. (9–10) show that the orbital and spin angular momentum operators enter in identically the same fashion in the wave equation, and as we have seen that they both transform in the same way in Kronig's reflection (15) it follows that inclusion of the spin does not destroy the invariance. But with its inclusion Kronig's number n must signify the total rather than just orbital parallel component of angular momentum, as the total is now what is involved in the symmetrical top. The observed combination of two x or two y levels cannot be attributed to the spin as conjectured by Hill and V. V., and is presumably due to perturbing external fields.

measure respectively the parallel components of orbital, spin, and total electronic angular momentum. Molecular spectral terms are classed of the S, P_i, D_i, F_i type according as $\sigma_l = 0, 1, 2, 3$. The value of the subscript i is that of σ and fixes the multiplet component. j and j_k measure the total angular momentum of the entire molecule, respectively inclusive and exclusive of spin. (j_k is used only in Hund's case b.) The magnetic quantum number m quantizes the component of j in the direction of an axis z' fixed in space. s is the spin quantum number which determines the spin angular momentum and has the values 0, 1/2, 1, . . . in singlet, doublet, triplet . . . spectra. l is roughly equal to the orbital electronic angular momentum, which is constant only if the non-centralness is negligible. Unlike the recent Hund-Wigner-Witmer scheme, this l does not include the essentially nuclear contribution due to molecular rotation. v is the vibrational quantum number, and n denotes the totality of electronic quantum numbers other than the σ's. We throughout use the letter B to denote the expression $h^2/8\pi^2 Mr.^2$ All symbols written in bold-face type in section 2 are operators, and in later sections are vectors.

2. Calculation of the Perturbing Matrix Elements

Stationary Molecules. We suppose the reader familiar with Pauli's[10] scheme of representing the spin in a system of f electrons by means of 2^f wave functions

$$\begin{aligned} &\Phi_{\alpha_1 \cdots \alpha_f},\ \Phi_{\beta_1 \alpha_2 \cdots \alpha_f},\ \Phi_{\alpha_1 \beta_2 \cdots \alpha_f},\ \cdots,\ \Phi_{\alpha_1 \alpha_2 \cdots \beta_f}, \\ &\Phi_{\beta_1 \beta_2 \alpha_3 \cdots \alpha_f},\ \cdots,\ \Phi_{\alpha_1 \cdots \alpha_{f-2} \beta_{f-1} \beta_f},\ \cdots,\ \Phi_{\beta_1 \beta_2 \cdots \beta_f}. \end{aligned} \tag{1}$$

The subscripts α_k and β_k correspond to the spin axis of the kth electron being quantized respectively parallel and antiparallel to the z-axis, which we throughout suppose to coincide with the axis of figure of the molecule. If a solution could be obtained in which each individual spin axis was quantized separately relative to the z-axis, only one of the wave functions (1) would need to be different from zero, but usually the magnetic interaction between the spins and the orbital angular momentum makes this impossible, and so requires 2^f simultaneous wave functions (1), the square of the modulus of any one of which can be regarded as the probability of the corresponding orientation of the spin axes. A stationary molecule will have 2^f simultaneous wave equations of the form

$$(\boldsymbol{H}_0 - W_0)\Phi_{i_1 \cdots i_f} = 0 \quad \text{with} \quad i_k = \alpha_k \quad \text{or} \quad \beta_k. \tag{2}$$

where $\boldsymbol{H}_0$ is an operator function of the coordinates $x_1, \cdots, y_1 \cdots z_1 \cdots z_f$ of the f electrons, and also of the Pauli spin operators $\mathbf{s}_{1x} \cdots$, $\mathbf{s}_{1y} \cdots$, $\mathbf{s}_{1z} \cdots \mathbf{s}_{fz}$ corresponding to the x, y, z, components of angular momentum of the various electrons. These operators have the following properties:

[10] W. Pauli, Jr., Zeits. f. Physik **43**, 601 (1927), especially p. 620 ff. Our spin operators (3) differ by a factor 1/2 from Pauli's, as his unit of angular momentum is $h/4\pi$.

$$\begin{aligned} s_{kz}\Phi_{\alpha_1\cdots\alpha_k\cdots} &= \tfrac{1}{2}\Phi_{\alpha_1\cdots\beta_k\cdots}, & s_{ky}\Phi\cdots_{\alpha_k}\cdots &= -\tfrac{1}{2}i\Phi\cdots_{\beta_k}\cdots, \\ & & s_{kz}\Phi\cdots_{\alpha_k}\cdots &= \tfrac{1}{2}\Phi\cdots_{\alpha_k}\cdots \\ s_{kz}\Phi\cdots_{\beta_k}\cdots &= \tfrac{1}{2}\Phi\cdots_{\alpha_k}\cdots, & s_{ky}\Phi\cdots_{\beta_k}\cdots &= +\tfrac{1}{2}i\Phi\cdots_{\alpha_k}\cdots, \\ & & s_{kz}\Phi\cdots_{\beta_k}\cdots &= -\tfrac{1}{2}\Phi\cdots_{\beta_k}\cdots. \end{aligned} \tag{3}$$

The inter-nuclear distance r will also be involved as a parameter in H_0. To include explicitly the coordinate arguments, usually omitted for brevity, we would thus write the first wave function, for instance, of (1), as $\Phi_{\alpha_1\cdots\alpha_f}(x_1, \cdots, y_1, \cdots, z_1, \cdots, z_f, \mathrm{r})$.

Rotating molecules. The wave equations for an actual molecule with moving nuclei are[11]

$$\left[H_0 - \frac{h^2}{8\pi^2 M r^2}\left(\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \cot\theta\frac{\partial}{\partial\theta} + \frac{\partial^2}{\partial\theta^2} + \operatorname{cosec}^2\theta\frac{\partial^2}{\partial\omega^2}\right) - W\right]\psi_{i_1'\cdots i_f'} = 0 \tag{4}$$

$$(i_k' = \alpha_k' \text{ or } \beta_k')$$

where θ and ω are the polar and azimuth angles specifying the position of the axis of figure relative to a fixed coordinate system x', y', z', and where M is the "reduced mass" $M_1 M_2/(M_1+M_2)$ of the nuclei. On the other hand H_0 is most readily expressed in terms of the x, y, z reference system which has the z axis parallel to the axis of figure, and which hence travels with the nuclei. H_0 is, of course, the same function of these moving coordinates, and related operators, as in (2). It would, of course, also be possible to express H_0 in the fixed reference system, but then H_0 would involve θ and ω explicitly inasmuch as the axis of figure is in general obliquely located in this system, and its position is involved in the potential energy binding the electrons to the nuclei. We suppose the mutual potential energy $Z_1 Z_2 e^2/r$ of the nuclei incorporated in H_0 and hence it does not appear explicitly in (4). Without loss of generality we may suppose the x axis to lie in the $x'y'$ plane. Then the moving and fixed axes are connected as follows

$$\begin{gathered} x = y'\cos\omega - x'\sin\omega, \quad y = z'\sin\theta - (x'\cos\omega + y'\sin\omega)\cos\theta \\ z = z'\cos\theta + (x'\cos\omega + y'\sin\omega)\sin\theta. \end{gathered} \tag{5}$$

Following Born and Oppenheimer,[2] also Kronig,[6] but with the generalization to include spin, we now seek approximate solutions of the form $\psi = \Phi\chi(r, \theta, \omega)$ where $\Phi(x_1 \cdots z_f)$ is what we shall term an "internal" wave function, i.e. a solution for the stationary molecule, and χ is a function of the nuclear coordinates alone. In performing the explicit differentiation with respect to the polar coordinates in (5), Φ must be regarded as a function

[11] The origin of all coordinate systems we suppose to be at the molecule's center of mass, which we assume is at rest. We thus neglect the molecule's translational energy, which enters in a trivial additive fashion. Also we neglect the difference between the center of mass of the molecule and of the nuclei. The inclusion of this difference would add only small terms of the order m/M times the ordinary rotational and vibrational energies, where m is the mass of an electron.

of r, θ, ω as this differentiation is to be performed under the assumption that the electronic coordinate axes are fixed in space, and by (5) the transformation from the moving axes used in (1–2) to fixed axes will cause the entrance of θ, ω.

It is particularly to be noted that in (4) we use a set of subscripts involving the $\alpha's$ and $\beta's$ rather than $\alpha's$ and $\beta's$. This is to indicate that we are using an x', y', z' rather than x, y, z system of reference for the Pauli wave functions, . . . i.e. referring the quantization of the spin relative to the fixed rather than moving system. This is, of course, necessary because (4) presupposes a fixed system of reference. It is thus necessary to transform our spin solution from the α, β to the α', β' system. Without this transformation we would neglect entirely the gyroscopic effect of the spin on the molecular rotation. The desired transformation is accomplished by means of the Cayley-Klein parameters and is explained in Pauli's paper. Pauli's angles Φ, θ are the same as $-(\omega+\frac{1}{2}\pi)$, $-\theta$ in our system and his third Eulerian angle Ψ is zero, as we suppose the x axis to fall in the x' y' plane. He formulates the transformation scheme for one electron, but the extension to any number furnishes no difficulty, as there is a simple superposition of the coefficients for the individual electrons, as already given by Neumann and Wigner.[12] The generalized Pauli transformation scheme, with one minor correction which appears necessary,[13] is

$$\Phi_{i_1'\cdots i_f'}=\sum_{i_1\cdots i_f} A(i_1'\cdots i_f';i_1\cdots i_f)\Phi_{i_1\cdots i_f}(x_1,\cdots,y_1\cdots,z_1,\cdots,z_f) \quad (6)$$

where the summation extends over the two values α_k and β_k for each i_k, and

$$A(i_1\cdots i_f';\, i_1\cdots i_f)=A(i_1';\, i_1)A(i_2';\, i_2)\cdots A(i_f';\, i_f) \quad (7)$$

with

$$\begin{aligned} A(\alpha_k';\,\alpha_k)&=\cos\tfrac{1}{2}\theta e^{-i\Omega/2}, & A(\alpha_k';\,\beta_k)&=-i\sin\tfrac{1}{2}\theta e^{-i\Omega/2}\\ A(\beta_k';\,\alpha_k)&=-i\sin\tfrac{1}{2}\theta e^{i\Omega/2}, & A(\beta_k';\,\beta_k)&=\cos\tfrac{1}{2}\theta e^{i\Omega/2}. \end{aligned} \quad (8)$$

Ω is an abbreviation for $\omega+\frac{1}{2}\pi$. By means of (6–7–8) the differentiation of the internal wave function with respect to ω and θ may now be performed. Thus

$$\frac{\partial\Phi'}{\partial\omega}=\sum_{k=1,\cdots,f}\left(\frac{\partial x_k}{\partial\omega}\frac{\partial}{\partial x_k}+\frac{\partial y_k}{\partial\omega}\frac{\partial}{\partial y_k}+\frac{\partial z_k}{\partial\omega}\frac{\partial}{\partial z_k}\right)\Phi'-\frac{1}{2}i\Phi'\sum c_k'$$

[12] J. V. Neumann and E. Wigner, Zeits. f. Physik **47**, 203; **49**, 73 (1928).

[13] It is necessary to interchange Pauli's S and S^{-1}. In other words the coefficients in his development (12a) of the ψ''s in the ψ's are S_{11}, S_{12}, S_{21}, $S_{22}=\alpha,\gamma,\beta,\delta$, rather than the inverse $\alpha^*,\beta^*,\gamma^*,\delta^*$. It is easily verified that without this correction the matrices which he defines at the bottom of p. 609 do not transform in the fashion (11), p. 612, from one coordinate system to another. Apparently the reason for the modification is that Ss_xS^{-1} gives the elements of s_x in the α', β' system rather than s_x' in the α, β system. The same correction is apparently needed in other literature, though not in Darwin's paper[28] on Dirac's theory, which has the same modification as ours.

where c_k' equals $+1$ or -1 according as i_k' equals α_k' or β_k', and where we have for brevity written Φ' for $\Phi_{i_1'\ldots i_f'}$. The first right-hand term results because by (5) the arguments $x_1, \cdots, z_f$ of Φ involve ω and the second term results from the dependence of the coefficients in the expansion (6) upon ω. This second term can be simply expressed by means of the Pauli spin operators, as by (2) $\frac{1}{2}\Phi'\Sigma c_k' = \sum \mathbf{s}_{zk}'\Phi'$ where $\mathbf{s}_{zk}'$ is similar to $\mathbf{s}_{zk}$ except that it refers to the primed system. If we use (5) and the relation $\mathbf{s}_{zk}' = \mathbf{s}_{zk}\cos\theta + \mathbf{s}_{yk}\sin\theta$ we find that

$$\partial\Phi'/\partial\omega = -i(\boldsymbol{P}_z\cos\theta + \boldsymbol{P}_y\sin\theta)\Phi'$$

with

$$\boldsymbol{P}_z = \sum_{k=1,\cdots,f}[-i(x_k\partial\cdot\cdot/\partial y_k - y_k\partial\cdot\cdot/\partial x_k) + \mathbf{s}_{z_k}] \tag{9}$$

and analogous definitions of $\boldsymbol{P}_x$ and $\boldsymbol{P}_y$. The operator $\boldsymbol{P}_z$ corresponds to the total combined orbital and spin electronic angular momentum about the z-axis, i.e., the axis of figure.

In like manner it is easily seen that $\partial\Phi'/\partial\theta = -i\boldsymbol{P}_x\Phi'$, and consequently the complete wave equations (4) become

$$\left\{H_0 - \frac{h^2}{8\pi^2 M}\frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \cot\theta\left(\frac{\partial}{\partial\theta} - i\boldsymbol{P}_x\right) + \left(\frac{\partial}{\partial\theta} - i\boldsymbol{P}_x\right)^2 + \operatorname{cosec}^2\theta\left(\frac{\partial}{\partial\omega} - i\sin\theta\boldsymbol{P}_y - i\cos\theta\boldsymbol{P}_z\right)^2\right] - W\right\}\psi_{i_1'\ldots} = 0. \tag{10}$$

Here in the differentiations with respect to θ and ω, only the explicit dependence of Ψ on θ, ω is to be considered, and not the implicit effects resulting from the appearance of these angles in the transformation from the moving to the fixed system. In case $\Psi = \Phi\chi(r,\theta,\omega)$ this means that $\partial/\partial\theta$, $\partial/\partial\omega$ operate only on the factor χ, but this restriction on the form of Ψ is unnecessary.

It is possible to construct a solution of the customary form[14]

$$\psi_{i_1'\ldots} = \Phi'(x_1, \cdots, z_f; r)R(r)u(\theta,\phi) \tag{11}$$

if one neglects certain terms, viz.,

$$\frac{h^2 i}{8\pi^2 M r^2}\left[\cot\theta(\boldsymbol{P}_x - i\boldsymbol{P}_y\boldsymbol{P}_z - i\boldsymbol{P}_z\boldsymbol{P}_y) + 2\operatorname{cosec}\theta\boldsymbol{P}_y\frac{\partial}{\partial\omega} + 2\boldsymbol{P}_x\frac{\partial}{\partial\theta}\right]\psi_{i_1'\ldots} \tag{12}$$

and the "high frequency" part of the expression

$$\frac{h^2}{8\pi^2 M r^2}\left[(\boldsymbol{P}_x^2 + \boldsymbol{P}_y^2)\Phi' - 2r\frac{\partial\Phi'}{\partial r} - r^2\frac{\partial^2\Phi'}{\partial r^2} - \frac{2r^2}{R}\frac{\partial R'}{\partial r}\frac{\partial\Phi'}{\partial r}\right]Ru \tag{13}$$

[14] In verifying Eqs. (12–15) it is well to remember that the P operators do not commute among themselves in multiplication, but being functions only of the internal coordinates, do commute with all functions, operator or otherwise, of the variables r, θ, ω. Because the P's do not commute, $\boldsymbol{P}_x\boldsymbol{P}_z\Phi'$ is by (20) $(\sigma \pm 1)\boldsymbol{P}_x\Phi'$ rather than $\sigma\boldsymbol{P}_x\Phi'$, with an analogous formula for the y component.

i.e. the part of (13) which vanishes on averaging over the frequencies connected with the "electronic" quantum numbers n, σ. The construction of such an average consists in discarding all matrix elements not diagonal in n, σ. The matrix elements of (12) are entirely of this type, as the elements of P_x, P_y are entirely of the form $\Delta\sigma = \pm 1$ (see Eq. 20 below); while P_z has only $\Delta\sigma = 0$, and hence (12) disappears on averaging over the frequency connected with σ. Now by a well known theorem in perturbation theory, high frequency terms which average to zero contribute only to the second and higher order energies. Hence, if all the internal electronic (including spin) frequencies are really high, i.e. large compared to that of molecular rotation, one can as a first approximation neglect (12) and the fluctuating part of (13). One then finds that the factors in (11) satisfy respectively the differential equations (1) and

$$\left[\frac{h^2}{8\pi^2 M r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+W-W_0(r)-W_{\text{rot}}(r)-W_{13}(r)\right]R=0 \tag{14}$$

$$\frac{h^2}{8\pi^2 M r^2}\left[\cot\theta\frac{\partial}{\partial\theta}+\frac{\partial^2}{\partial\theta^2}+\operatorname{cosec}^2\theta\left(\frac{\partial}{\partial\omega}-i\sigma\cos\theta\right)^2\right]u+W_{\text{rot}}u=0 \tag{15}$$

In writing (15) we have utilized the relation $P_z\Phi' = \sigma\Phi'$, as the total combined orbital and spin angular momentum of the electrons about the axis of figure has the constant quantized value σ in a stationary molecule. The term $W_{13}(r)$ in (14) denotes the time average[15] of (13) over the internal motion of the electrons. As the coefficient of u in (13) involves neither θ nor ω, $W_{13}(r)$ is independent of the rotational quantum numbers j, m, and the effect of $W_{13}(r)$ is very approximately merely the same as changing the internal energy levels W_0 by relatively small amounts $W_{13}(r_0)$.

Eq. (14) is that governing the vibrational excitation of the molecule, which the present paper does not purport to treat. About all we shall need to know is that its solution R falls off in a rapid, exponential fashion from the maximum magnitude of R at $r = r_0$. Here r_0, the "equilibrium internuclear distance," is the value of r which minimizes $W_0(r_0)$, or more accurately in a moving molecule $W_0 + W_{\text{rot}} + W_{13}$. The characteristic values of (1) and (15), also the average of (13), involve r as a parameter, so that $W_0 + W_{\text{rot}} + W_{13}$ plays the rôle of a sort of potential function in (14).

Eq. (15) is that of the "symmetrical top." Reiche and Rademacher,[16] also Kronig and Rabi,[17] have shown that its characteristic values are

$$W_{\text{rot}} = B[j(j+1)-\sigma^2] \qquad (B = h^2/8\pi^2 M r^2) \tag{16}$$

[15] This time average is, of course, a diagonal element of the matrix which represents (13) for the internal motion of the electrons, The diagonal elements coming from the first and third terms of (13) do not in general vanish, but those coming from the second and fourth terms can be proved equal to zero.

[16] F. Reiche and H. Rademacher, Zeits. f. Physik **39**, 444 (1926); **41**, 453 (1927).

[17] R. de L. Kronig and I. I. Rabi, Nature **118**, 805 (1926); Phys. Rev. **29**, 262 (1927).

The energy levels (16) were also derived yet earlier by Dennison[18] with matrices. If we use one of the formulas for Jacobian polynomials,[19] the characteristic functions of (15), normalized to unity, are

$$u_{d s p}(t,\omega)=\left[\frac{(d+s+p)!(1+d+s+2p)!}{p!(d+p)!(s+p)!2\pi t^{d}(1-t)^{s}}\right]^{1/2}\frac{d^{p}}{dt^{p}}\left[t^{d+p}(1-t)^{p+s}\right]e^{im\omega} \qquad (17)$$

where

$$t=\tfrac{1}{2}(1-\cos\theta),\quad s=|m+\sigma|,\quad j=\tfrac{1}{2}(d+s)+p,\quad d=|m-\sigma|. \qquad (18)$$

The quantum numbers j, m, etc. are as explained at the end of section 1.

The derivation of (16) without the electron spins is an old story.[2,6] Our new result is that it is valid with spins, σ now denoting the combined spin and orbital angular momentum about the axis of figure. The reason for this is, of course, that Eqs. (9–10) show that the spin and orbital electronic angular momenta modify the equations of molecular rotation in exactly similar additive fashions. This identity of the spin and orbital gyroscopic effects seems only reasonable, and has commonly been assumed in band spectra without proof. It is, however, perhaps of some interest to have verified this similarity by use of the Pauli spin wave functions, for the spin effects are transformed from the fixed to moving coordinate systems by means of a method of expansion involving the Cayley-Klein parameters, wh ch is at least superficially different from the method of transforming the orbital effects by the simple substitution (5) in the coordinate arguments. (This apparent dissimilarity in the spin and orbital transformations could, however, be removed by using Winger's[12] group theory treatment of rotations.) It is, of course, necessary to give σ, j, m all half-integral values in molecules with an odd number of electrons. This clearly does not affect the analytic character of the t part of the solution, for by (18) s, p, d still remain integral, and so the hypergeometric series encountered in solving (15) still reduces to a Jacobian polynomial for the characteristic values (16). At first sight it appears as though the factor $e^{im\omega}$ with half-integral m in (17) would destroy the single-valuedness of ψ_{ii}'. . . . However, Eqs. (7–8) show that the explicit expansion (6) of Φ' introduces factors of each term of the form $e^{iq\omega/2}$ where q is an odd or even integer according as is the total number f of electrons. Thus by (11) the appearance of the half-quantum numbers associated with the spin does not destroy the single-valued, analytic character of the wave function, contrary to the impression which is obtained[17] when the simple symmetrical top model is used without investigating the transformation properties of the Pauli wave functions. The persistence of characteristic functions of the form (18) shows that the Hönl-London intensity formulas, ordinarily proved rigorously only for singlets, also apply to multiplet spectra provided the motion is close enough to Hund's ideal case (a) so that the neglected terms (12–13) are unimportant. Otherwise

[18] D. M. Dennison, Phys. Rev. **28**, 318 (1926).

[19] Courant-Hilbert, Methoden der Mathematischen Physik, p. 75, Eq. (55′).

(as in his case b) the "unperturbed" characteristic values and functions (16–17) cease to be good approximations (cf section 3).

We must now seek to take into account the omitted terms (12). This is probably best done by calculating the matrix elements. Doubtless there are readers of the category who have a peculiar abhorence of any mention of the word "matrices," but the perturbation theory even in the purest wave language is substantially equivalent, and the matrix elements can be regarded as simply convenient designations for certain quadratures involving the wave functions which are inevitably encountered, as they are the coefficients of the development of $f\psi$ in a series of orthogonal functions. The neglected part (12) may be regarded as adding a perturbative potential ("Störungsfunktion") whose matrix elements are

$$H_1(n\sigma vj\,;n'\sigma'v'j') = \sum_{i_1'\cdots i_f'} \int\cdots\int \psi^*_{ai_1'\ldots i_f'} f\psi_{a'i_1'\ldots i_f'} dx_1\cdots dz_f r^2 dr dt d\omega \quad (19)$$

where a denotes the totality of subscripts $n\sigma vjm$, while $f\psi$ is an abbreviation for the entire expression (12). As previously, the sum is over the two values α_k' and β_k' for each i_k', and $\psi_{i_1'}$. has the unperturbed value (11). We throughout suppose each of the factors of (11) norma ized to unity, and use the asterisk to denote the conjugate imaginary. As stated in the introduction, the single index n designates all the electronic quantum numbers other than σ, while v is the vibrational quantum number. Although we are now taking into account (12) we continue to neglect the periodic part of (13). We do this as (13) gives exclusively elements which are not only independent of the amount of rotation j, but also are diagonal[20] with respect to σ. Hence the periodic part of (13) is of no interest in the rotational distortion and sigma-doubling effects considered in the present paper.

We shall consider separately, and in order, the effect of integrating in (19) over the electronic or internal coordinates $x_1, \cdots, z_f$ the vibrational coordinate r and the rotational coordinates t, ω. The effect of the internal integration, which is to be construed as including the sum over the various spin wave functions, is to replace the P operators by the matrices $P_q(n\sigma; n'\sigma')$ ($q = x$, y, or z) giving the components of total electronic angular momentum in a stationary molecule. The z-component, as mentioned in the introduction is a diagonal matrix of the form $P_z(n\sigma;\ n\sigma) = \sigma$. The elements of P_x and P_y vanish unless $\sigma' = \sigma \pm 1$, and are of equal absolute magnitude owing to the parity of the two coordinate axes perpendicular to the figure axis. Their phase relations are such that

$$P_x(n\sigma\ ;n'\sigma\pm 1) = \mp iP_y(n\sigma\ ;n'\sigma\pm 1) \quad (20)$$

These are all well-known selection principles connected with quantization

[20] The diagonality with respect to σ of the matrix elements corresponding to the first term of (13) follows from the phase relations (20). Such diagonality of the remaining part of (13) is an easy consequence of the fact that Φ involves the angle ϕ_1 defined in footnote 21, only through the factor $e^{i\sigma\phi_1}$.

about an axis of symmetry, and are readily established[21] from the fact that there is an ignorable coordinate connected with rotation about such an axis.

The effect of integrating over r is to replace $h^2P_y(n\sigma;\ n'\sigma')/8\pi^2Mr^2$ by

$$(BP_y)(n\sigma v\ ;\ n'\sigma'v') = \int_0^\infty R_{nv}^*[P_y(n\sigma\ ;\ n'\sigma')h^2/8\pi^2Mr^2]R_{n'v'}r^2dr \qquad (21)$$

with $B=h^2/8\pi^2Mr^2$, and with an analogous formula for the x component. If the electronic quantum numbers n, σ do not change except for different orientations of the spin, then as the forces exerted by the spin moment are relatively small, the equilibrium internuclear distances will be very nearly[22] the same in the initial and final states, and R_{nv} and $R_{n'v'}$ will belong to the same set of orthogonal functions which vanish except in the vicinity of a common maximum point $r=r_0$. This makes (21) very approximately a diagonal matrix with respect to v whose elements are

$$(BP_y)(n\sigma\ ;\ n'\sigma') = \delta(v,v')P_y(n\sigma\ ;\ n'\sigma')B_0, \quad B_0=h^2/8\pi^2Mr_0^2 \qquad (22)$$

where $P_x(n\sigma;\ n'\sigma')$ and $P_y(n\sigma;\ n'\sigma')$ (which unlike P_z, depend on r) are to be evaluated with $r=r_0$. The expression δ equals unity if its arguments are equal and vanishes otherwise. If the orbital electronic quantum numbers are different in the initial and final states, the equilibrium moments of inertia in these states will differ, and R_{nv} and $R_{n'v'}$ will belong to different sets of orthogonal functions, so that (21) cannot in general be simplified. However, it may happen that the vibrational excitation in the state n is small. Then as first mentioned by Condon[23] in discussing Franck's theory of electron jumps in molecular spectra, the amplitudes associated with

[21] Let ρ_k, z_k, ϕ_k be the cylindrical coordinates of an electron, referred to the axis of figure of the molecule, and let $\gamma_k=\phi_k-\phi_1 (k=2,\cdots,f)$. If, first we neglect the spin, then it is easily seen that the internal characteristic functions are of the form $e^{i\sigma\phi_1}f(\gamma_2,\cdots,\rho_1\cdots,z_1,\cdots)$ (cf. Kronig[6]). Without the spin P equals l, and on shifting to our cylindrical coordinates the differential operators for l_x etc. given in footnote 9, it is found that because of the exponential factor the matrix elements of l_x, l_y vanish unless $\sigma'=\sigma\pm1$ and that the phase relations are as given by (20). If we now seek to include the spin, we must add the Pauli spin operators to the orbital differential operators to get the total angular momentum operators. The selection rules are then easily proved to remain valid in virtue of the definitions (3) and the fact that if the total angular momentum is conserved, $\Phi_{i_l}\cdots$ involves ϕ_1 through a factor $e^{i\sigma_l\phi_1}$ where $\sigma_l=\sigma-\frac{1}{2}\Sigma c_k$ with c_k defined as after Eq. (8).

Most of the literature (including the orginal Heisenberg-Jordan paper) has $\pm i$ where we have $\mp i$ in (20). This would mean that in the state σ the wave function had (neglecting spin) a factor $e^{-i\sigma\phi_1}$ rather than $e^{i\sigma\phi_1}$, which appears legimate only if the momentum operators are defined as $ih\partial\cdots/\partial q$ rather than $h\partial\cdots/i\partial q$ or if the matrix elements are defined as having the asterisk attached to the second rather than first wave function of (19), but these are not the usual conventions such as we use. The formulas for the matrix elements of the spin angular momentum which Pauli gives at the bottom of p. 609 show that his convention on phases is the same as ours, so that (20) applies to both orbital and spin effects (in this connection one must be careful to examine the sign of Pauli's $(s_y)_{nm}$ rather than his operator s_y).

[22] Throughout the paper we neglect the slight dependence of the moment of inertia on the spin quantization σ_s, also its dependence, likewise slight, on j due to centrifugal expansion.

[23] E. U. Condon, Proc. Nat. Acad. Sci. **13**, 462 (1927).

transitions to other electronic states n will be appreciable only if they have such large vibrational excitation that $R_{n'v'}$ falls off relatively slowly away from its maximum at $r=r_0'$, and so "overlaps" the sharp peak of R_{nv} at r_0. In such a case one can without much error take the bracketed factor in (21) outside the integration, evaluating it at $r=r_0$, and then (21) simplifies into

$$(BP_y)(n\sigma v\ ;\ n'\sigma'v')=BP_y(n\sigma\ ;\ n'\sigma')a(nv\ ;\ n'v') \tag{23}$$

where the $a(nv;\ n'v')$ are the coefficients of the development of $R_{n'v'}$ in the R_{nv}, i.e., the values of the right side of (21) when the bracketed factor is deleted. Since both the R_{nv} and $R_{n'v'}$ are normalized orthogonal sets, the a's form a unitary matrix, making

$$\sum_{v'}a(nv\ ;\ n'v')a^*(nv''\ ;\ n'v')=\delta(v,v''),\quad a(nv\ ;\ n'v')=a^*(n'v'\ ;\ nv) \tag{24}$$

In view of all the foregoing, Eq. (19) now becomes

$$H_1(n\sigma vj\ ;\ n'\sigma\pm 1v'j')=(BP_y)(n\sigma v\ ;\ n'\sigma\pm 1v')\int\int g(t,\omega)dtd\omega \tag{25}$$

with

$$g(t,\omega)=u^*_{d''s''p''}\left[\frac{1}{t^{1/2}(1-t)^{1/2}}\left((\sigma\pm 1)(1-2t)+i\frac{\partial}{\partial\omega}\right)\pm 2t^{1/2}(1-t)^{1/2}\frac{\partial}{\partial t}\right]u_{d's'p'}$$

where d'', s'', p'' are the values of d, s, p associated by (18) with σ, j, m, and d', s', p' are those associated with $\sigma\pm 1$, j', m'. The integration over ω shows us immediately that $m=m'$. The integration over t is slightly more difficult, but is readily effected if one uses the following relations

$$H_1(n\sigma vj\ ;\ n'\sigma\pm 1v'j')=H_1{}^*(n'\sigma\pm 1v'j'\ ;\ n\sigma vj) \tag{26}$$

$$\frac{dU_{dsp}}{dt}=\frac{1}{2}\left[\frac{s}{1-t}-\frac{d}{t}\right]U_{dsp}+\left[\frac{(d+s+p)(p+1)}{t(1-t)}\right]^{1/2}U_{d-1s-1p+1} \tag{27}$$

$$=\frac{1}{2}\left[\frac{s}{1-t}+\frac{d}{t}\right]U_{dsp}-\left[\frac{(p+s)(d+p+1)}{t(1-t)}\right]^{1/2}U_{d+1s-1p}$$

Eq. (26) merely expresses the Hermitian property, which is to be expected with proper normalization, and halves the number of terms to be calculated. Since the matrices (BP) are surely Hermitian, (26) is obtained by partial integration of (25) without using the special properties (17) of the u's. The relations (27) are identities following from the definition (17), with the notation U for the function $(2\pi)^{1/2}\ ue^{-im\omega}$ which has no factor involving ω[24]. By means of (26–27) the integrand of (25) can be reduced, after integrating over ω, to an expression of the form $CU^*_{dsp_1}U_{dsp_2}$, where C is independent of t but not of d, s, p_1, p_2. In virtue of the orthogonality and normalization of the U's, the integral of such an expression is C when $p_1=p_2$ and

[24] The factor $(2\pi)^{1/2}$ is included to make U normalized to unity when the normalizing integral is taken over t alone, whereas that for u is to be taken over both t and ω. We suppose the normalization relative to the element of integration dt rather than $\sin\theta d\theta=2dt$.

zero otherwise. The values of p_1, p_2 and the manipulation in the reduction, depend on the particular form assumed by the connecting relations, (17) which is influenced by the signs and relative magnitudes of m and σ. The first and second forms of (27) are respectively useful according as σ is numerically greater or smaller than m. When, however, one shifts back to the σ, j, m notation the result is in all cases (barring a trivial question of sign[25])

$$H_1(n'\sigma vj\ ;\ n'\sigma'v'j')=0 \qquad \text{unless} \qquad \sigma'=\sigma\pm 1, \qquad j'=j \tag{28}$$

$$H_1(n\sigma vj\ ;\ n'\sigma\pm 1v'j)=2(BP_v)(n\sigma v\ ;\ n'\sigma\pm 1v')\left[(j+\tfrac{1}{2}-\bar{\sigma})(j+\tfrac{1}{2}+\bar{\sigma})\right]^{1/2} \tag{29}$$

where $\bar{\sigma}$ denotes the mean $\sigma\pm 1/2$ of the initial and final values of σ. This is the final answer, and is essentially similar to Kronig's[6], except for some simplifications resulting from our use of (20), etc. The diagonality with respect to j expressed in (28) could have been suspected from kinematical considerations, as a precession of the entire molecule about the "invariable axis" of total angular momentum such as is associated with the quantum number j will not affect the magnitude of the interaction between the electronic and rotational angular momentum. The complete independence of (29) of the magnetic quantum number m is, of course, due to the arbitrariness of spacial orientation.

Dirac's "quantum theory of the electron." Ostensibly we use throughout Pauli's scheme of two wave functions per electron. According to Dirac's newer "quantum theory of the electron,"[26] there are presumably four wave functions per electron, although the extension of the Dirac theory to systems with more than one electron has yet to be given. It is, however, only reason-

[25] If the rotational characteristic function is defined in precisely the fashion (17) a minus sign must be inserted before the right hand side of (29) in the domain $m>\bar{\sigma}$. Such a difference is of no consequence, as by examination of (25) it is seen that the sign can be made positive throughout by altering the sign in the definition of some of the characteristic functions. This is legitimate because they have each an arbitrary phase factor of modulus unity. To make the sign positive throughout, as assumed in writing (29), the characteristic functions u' which must be used are $u'=(-1)^{\sigma}u$ for $m\gtrless\bar{\sigma}$ and $u'=(-1)^{m}u$ for $\bar{\sigma}\gtrless m$, where u is defined as in (17). As it is easily seen from (29) that $u_{d_{sp}}(t)=(-1)^{p}u_{id_{sp}}(1-t)$, it follows that $u'(j,\sigma,m,t)=(-1)^{j+m}u'(j,-\sigma,m,1-t)$. In the rotational characteristic functions u'' which Kronig uses he supposes that $u''(j,\sigma,m,t)=(-1)^{j+m+\sigma}u''(j,-\sigma,m,1-t)$. This implies that $u''=u$ for $\sigma/m\leqq 0$, $u''=(-1)^{\sigma}u$ for $0\leqq\sigma/m\leqq 1$, $u''=(-1)^{m}u$ for $\sigma/m>1$. Such a definition inserts a negative sign into the right side of (29) for $\sigma<0$ and with Kronig the right side of (29) changes sign with σ. There is thus agreement with Kronig when the phase factors are considered, and his combination relations, of course, apply when we are careful to discriminate between the symmetric and antisymmetric states. He does not, however, mention these peculiarities of sign in his definition of the characteristic functions.

It is to be noted that (29) does not involve the spacial quantum number m. This is just what we should expect, as the energy cannot depend on spacial orientation in the absence of external fields. If this independence of orientation be accepted at the oustset, it is only necessary to make the calculation for one particular value of m. As Witmer notes in connection with a somewhat different problem, (Proc. Nat. Acad. Sci. 13, 60, 1928) the special case $j=m$ is particularly easy, since here by (18) $p=0$. It is, however, a rather satisfying check to have verified that m does drop out in the general case.

[26] P. A. M. Dirac, Proc. Roy. Soc. **117A**, 610; **118A**, 351 (1928).

able to suppose that an extended theory would possess the following features: (a) the terms representing the kinetic energy of the nuclei enter in the Hamiltonian, at least very approximately, in an additive fashion with the ordinary electrostatic potential energy term,[27] (b) that the transformation cofficients in rotation can be obtained as in Eq. (7) by superposition of those of individual electrons separately, and (c) that operators corresponding to spins of individual electrons are defined as in the one-electron case. The supposition (a), of course, neglects internal spins of the nuclei, but this is presumably a very high order effect still shrouded in obscurity. If one grants these premises, the use of four rather than two wave functions per electron occasions no difficulty in our work, for in a one-electron system each quartet of Dirac wave functions is separable into two pairs such that the members of each pair transform under a rotation independently of the other pair, and in exactly the same fashion as Pauli's two wave functions.[28] Thus by (b) even if we use 4^f rather than 2^f wave functions, each one of them in the x', y', z' system is still expressible in the fashion (6) as the sum of only 2^f wave functions in the x, y, z one. The passage from (6) to (10) proceeds as before because according to Dirac the spin angular momentum operators s_{xk} etc. work independently on each pair of the quartet in just the Pauli fashion. After Eq. (10) there are no modifications worth mentioning except that in the formula (19) for the matrix elements we must, of course, (unlike Eq. 6) sum over all 4^f wave functions. The final formulas (16–17) (28–29) ensue, and so all the results of the present paper hold with the Dirac theory.

3. Rotational Distortion of Spin Multiplets

In a stationary molecule the motion of the spin angular momentum s is very approximately that of a regular precession about the axis of figure. Following Heisenberg and Jordan's work[29] on the Zeeman effect, we may then take the non-vanishing matrix components of s to be

$$\pm i s_x(\sigma_s\sigma_s \pm 1) = s_y(\sigma_s\,;\,\sigma_s \pm 1) = \tfrac{1}{2}\left[s(s+1) - \sigma_s(\sigma_s \pm 1)\right]^{1/2} \qquad s_z(\sigma_s\,;\,\sigma_s) = \sigma_s \quad (30)$$

Actually, as will be shown on p. 492, the influence of the perpendicular component of orbital angular momentum distorts the precession and hence formulas (30), but this is a higher order effect important only in the later sections on sigma-doubling. In considering the effect of the molecular rotation on the spin motion, we need use only the spin part of the angular momentum P_y in (29). Actually $P_y = s_y + l_y$ but very approximately the terms coming from the orbital part l are independent of σ_s and have $\Delta\sigma_l = \pm 1$

[27] The writer is indebted to Dr. J. R. Oppenheimer for this suggestion regarding the additivity of the nuclear and potential energy terms.

[28] Cf. C. G. Darwin, Proc. Roy. Sec. **118A**, 656 (1928).

[29] Heisenberg and Jordan, Zeits. f. Physik **37**, 263 (1926). They applied to the spin the formulas for angular momentum first derived in the following reference. Besides the reversal of the sign of i explained in note 21, we use x,y axes differing by 90° from Heisenberg and Jordan's, so that our x,y are the same as their $y, -x$. We do this because it is convenient for the elements of the y component to be real in our work.

rather than $\Delta\sigma_s = \pm 1$. Using the independence of moment of inertia of spin expressed in (22), we may now consider the perturbation matrix (29) to be

$$H_1(\sigma_s\,;\,\sigma_s \pm 1) = B[j(j+1)-(\sigma_l+\sigma_s)(\sigma_l+\sigma_s\pm 1)]^{1/2}[s(s+1)-\sigma_s(\sigma_s\pm 1)]^{1/2} \quad (31)$$

The diagonal elements of the magnetic plus rotational energy are

$$H_0(\sigma_s\,;\,\sigma_s) = f(\sigma_s)+B[j(j+1)-(\sigma_l+\sigma_s)^2]+B[s(s+1)-\sigma_s^2] \quad (32)$$

Here $f(\sigma_s)$ is the ordinary so-called "magnetic energy" of interaction between the spins and orbital angular momentum. Of course f depends on the other electron quantum numbers n, σ_l, besides σ_s, but these are fixed within a multiplet and so not listed as arguments. If the ordinary "cosine-law" of coupling between s and the component of l parallel to the figure axis is applicable, then

$$f(\sigma_s) = A\sigma_l\sigma_s. \quad (33)$$

The second term of (32) gives the ordinary "symmetrical top" rotational energy (16). The third term of (32) is the contribution of s to the mean value W_{13} of the expression (13). As $P_x = s_x + l_x$, the first term of (13) involves s, and from (30) $s_x^2+s_y^2$ is a diagonal matrix $s(s+1)-\sigma_s^2$, while the average of $s_x l_x$ or $s_y l_y$ is zero, at least with the independence of spin and orbital precessions presupposed by (30). We have discarded the balance of W_{13}, as it is independent of σ_s.

If the frequency of molecular rotation is small compared to the spin multiplet frequency intervals, the energy can be developed as a power series in the ratio $\lambda' = B/A$, then small, of the orders of the molecular and magnetic energies. Well-known perturbation formulas[30] show that then the energy is to terms of the order λ'^2

$$W = H_0(\sigma_s\,;\sigma_s)+\frac{|\,H_1(\sigma_s\,;\,\sigma_s+1)\,|^2}{h\nu(\sigma_s\,;\,\sigma_s+1)}+\frac{|\,H_1(\sigma_s\,;\,\sigma_s-1)\,|^2}{h\nu(\sigma_s\,;\,\sigma_s-1)}\,. \quad (34)$$

The denominators $h\nu(\sigma_s;\sigma_s') = H_0(\sigma_s;\sigma_s) - H_0(\sigma_s'\,;\,\sigma_s')$ can by (32) be taken as $f(\sigma_s)-f(\sigma_s')$ to an adequate approximation since they enter only in second order terms. The values of the H elements in (34) can immediately be substituted from (31–32). If we then assume (33), the formulas so obtained for the three levels of the triplet case $s=1$ are those already given more explicitly on p. 261 of Hill and V. V. An interesting thing to note is that by (31) the two last terms in (34), which are the corrections for rotational distortion, involve j only through a factor $j(j+1)+C$ where C is independent of j but not of the multiplet component. This means that for any s the effect of rotational distortion is approximately, assuming the coupling always remains nearly type (a), simply to change the constants A' and B' in the conventional formula $A'+B'j(j+1)$ for molecular energy levels. As the

[30] Born, Heisenberg, and Jordan, Zeits. f. Physik **35**, 587 ff (1926).

constants by which $j(j+1)$ is multiplied in the correction terms of (34) depend on σ_s, A' and B' will have different values in the various multiplet components. Thus the apparent moment of inertia, deduced from experimental values of the constants A' and B' without care to resolve the rotational distortion, i.e. the last two terms of (34) from the first term, may have entirely different values in the various multiplet components, even though the true moment of inertia is very nearly the same. One further point is that regardless of whether the multiplet is "regular" or "inverted" the largest apparent moment of inertia B' always goes with the spin component of largest energy f. Hence comparison of the different values of B' will not tell whether a multiplet is regular or inverted.

It is to be emphasized that (34) is a good approximation only if the rotational distortion, which increases rapidly with j, is so small that Hund's case (a) (explained in the introduction) is a good approximation. An analagous development in $\lambda = 1/\lambda'$, valid instead near Hund's case (b), is given in Eq. (23) of Hill and V. V. In the general intermediate case between (a) and (b) standard matrix transformation theory shows that the energy levels are the roots of the "secular" determinant

$$\left| H(\sigma_s\,;\,\sigma_s') - \delta(\sigma_s\,;\,\sigma_s')W \right| = 0 \qquad \sigma_s, \sigma_s' = -s, \cdots, s \tag{35}$$

which yields an algebraic Eq. [31] for W of order $2s+1$. For the doublet case $s = 1/2$ this reduces to the simple formula[32]

$$W = \tfrac{1}{2}\left[f(-\tfrac{1}{2}) + f(\tfrac{1}{2})\right] + B\left[(j+\tfrac{1}{2})^2 - \sigma_l^2\right] \pm \tfrac{1}{2}\left[4B^2(j+\tfrac{1}{2})^2 + \Delta E(\Delta E - 4B\sigma_l)\right]^{1/2} \tag{36}$$

with ΔE denoting the spin doublet width $f(1/2) - f(-1/2)$ for a stationary molecule. If we assume the "cosine" law (33), which we now see is unnecessary, (36) is identical with Hill and V. V's formula (27) obtained by an entirely different method, in which the unperturbed system had the spin loosely coupled in Hund's fashion (b) and included the rotational rather than magnetic energy in the unperturbed Hamiltonian. In the doublet case the transformation matrix T associated with the determinant (35) can immediately be determined, and the effect of rotational distortion on intensities thereby determined by the familiar matrix formula $q = Tq_0T^{-1}$. The formulas for T are similar[5] to Hill and V. V's Eqs. (37–38) and the original unperturbed case (a) amplitudes q_0 are, of course, the Hönl-London

[31] It is doubtless possible to establish the general identity of the determinantal Eq. (35) with the corresponding Eq. (20) of Hill and V. V., instead of verifying numerically the agreement, as we do, only in the special cases $s = 1/2$, 1. Perhaps methods similar to those given by Schlapp (Proc. Roy. Soc. **119A**, 313, 1928) would be useful.

[32] Eq. (36) can be derived in a semi-theoretical manner without going through the labor of calculating the perturbing matrix (29) or (31) if we assume the diagonal elements to be given by (32), and if we grant that the off-diagonal elements are linear in B and independent of f. Then in the doublet case the magnitude of the needed perturbing element $H_1(-1/2;\ 1/2)$ is uniquely determined by the requirement that the formula for W yielded by the determinant (35) shall reduce to the well-known result $W = Bj_k(j_k+1) - B\sigma l^2$ in the limit $f = 0$ (Hund's case b).

ones given in Eq. (2) of Hill and V. V. The reader is referred to their paper for discussion of the superiority of (36) over the old quantum theory, and especially of intensity relations, including allowance in the latter for the fact that in electronic transitions the magnetic coupling strengths will be different in the initial and final states. As first noted by Mulliken,[33] Eq. (36) reduces rather fortuitously to the old Kramers-Pauli formula when $\Delta E = 2B\sigma_l$. The reader is referred to his paper for comparison of (36) with experiment.

4. Sigma-Type Doubling in Singlet States.

We shall first treat sigma-doubling in states which have zero resultant spin angular momentum and which hence belong to the singlet spectral system. Our procedure is superficially different from Kronig's, as we use an unperturbed solution corresponding to a constant angular momentum σ about the figure axis (i.e. a wave function involving the cyclic angle ϕ, defined in footnote 21 only through a factor $e^{i\sigma\phi_1}$) whereas Kronig uses a wave function which is a linear combination of those corresponding to angular momenta $+\sigma$ and $-\sigma$. In a one electron system this means that Kronig uses sines and cosines where we use exponentials. Kronig's method is probably the more elegant, as by dividing states into two classes which do not combine with each other in the Hamiltonian function he is able at the outset to remove the degeneracy difficulties coming from the identity of energies for $+\sigma$ and $-\sigma$ in the stationary molecule. It is, however, an alternative method, possibly of some interest, to keep as long as possible a solution corresponding to a constant angular momentum of uniform sign relative to the axis of figure. In fact the procedure is illustrative of a perturbation method when degeneracy is encountered only in higher approximations. We shall seek to develop the energy as a power series in $B = h^2/8\pi^2 Mr^2$, as is legitimate if the rotational frequencies are small compared to the internal electronic frequencies of the molecule. To a first approximation, i. e. terms of the order B, there is no difficulty with sigma-type degeneracy, as the perturbing matrix elements given by (29) have only $\Delta\sigma = \pm 1$ and so do not connect the states $+\sigma$ and $-\sigma$ if σ is an integer. We can then use the perturbation theory of non-degenerate systems, which tells us that to a first approximation the perturbing elements (29) have no effect on the energy, owing to the absence of diagonal elements, while the corresponding transformation matrix is $S = 1 + S_1$[34] with

$$S_1(n\sigma vj\ ;\ n'\sigma'v'j) = H_1(n\sigma vj\ ;\ n'\sigma'v'j)/h\nu(n\sigma vj\ ;\ n'\sigma'v'j) \tag{37}$$

where $\sigma' = \sigma \pm 1$ and $h\nu(n\sigma vj;\ n'\sigma'v'j) = H_0(n\sigma vj) - H_0(n'\sigma'v'j)$, while H_1 is

[33] R. S. Mulliken, Phys. Rev. **32**, 388 (1928).

[34] We write our series development as $1 + S_1 + \cdots$ rather then the more usual $1 + \lambda S_1 + \cdots$. The customary form could, of course, be obtained by multiplying the right side of (29) by λ. This, however, is unnecessary, for although B, being a matrix, cannot be used as an ordinary parameter, nevertheless the power to which its elements are raised identifies the order of approximation.

given by (29). The unperturbed energy H_0 we now and henceforth suppose *inclusive* of the vibrational and ordinary "symmetrical top" rotational energies associated with Eqs. (14–15–16), as well as of the internal energy, whereas in section 2 we used H_0 to denote just the internal energy of a stationary molecule. Use of (37) makes the transformed Hamiltonian

$$S(H_0+H_1)S^{-1}$$

a diagonal matrix only to a first approximation, i. e., if we keep the portion $H_0+S_1H_0-H_0S_1$ which is of order B or lower, and discard the remaining portion,

$$H_0S_1^2-S_1H_0S_1+S_1H_1-H_1S_1+\cdots.$$

To solve the problem to a second approximation we can regard this part as constituting a new perturbation matrix, which we may call[35] $H^{(2)}$, and which, if we do not go beyond B^2, will involve elements of the form $\Delta\sigma=0$ and $\Delta\sigma=\pm 2$. We can now, provided $\sigma>1$, again apply the perturbation theory of non-degenerate systems and find another, superposed, canonical transformation, which will make the Hamiltonian a diagonal matrix to terms of the order B^2. . . . . This process could be repeated indefinitely were it not for the complication that after applying the transformation of order $B^{2\sigma-1}$ we find that when we set up the new perturbing matrix $H^{(2\sigma)}$ of order $B^{2\sigma}$, it will contain "degenerate" elements of the form $H^{(2\sigma)}(n\sigma vj;\ n-\sigma vj)$ connecting states which up to this stage have been of identical energy. The explicit formula for these elements is a bit formidable appearing, but with the aid of conventional perturbation theory is seen to be[36, 37]

$$H^{(2\sigma)}(n\sigma v\,;\ n,\ -\sigma v)$$

$$=\sum_{n'v'n''v''\ldots n^xv^x}\frac{H_1(n\sigma v;n'\sigma-1v')H_1(n'\sigma-1v';n''\sigma-2v'')\cdots H_1(n^x,-\sigma+1v^x;n,-\sigma,v)}{h^{2\sigma-1}\nu(n\sigma v\,;\,n'\sigma-1v')\nu(n\sigma v';\,n''\sigma-2v'')\cdots\nu(n\sigma v\,;\,n^x,-\sigma+1,\,v^x)} \tag{38}$$

[35] Our $H^{(2)}, \cdots$ are not the same as Born, Heisenberg and Jordan's $H_2, \cdots$, as our expressions result from applying successive transformations to a Hamiltonian originally of the form H_0+H_1, whereas they consider the more general problem in which the perturbative potential has at the outset terms of higher order $H_2, \cdots$.

[36] In writing (38) and following expressions we assume the given number σ to be positive. This involves no loss of generality, as one end or other of the range $\sigma, \cdots, -\sigma$ under consideration must be positive.

[37] The product in the numerator of an expression such as (38) can be calculated neglecting entirely the sigma-type degeneracy for the "inner levels" $\sigma-1, \cdots, -\sigma+1$. In other words we can use in the numerator the values of the matrix elements which would be obtained without making for each of the inner levels transformations analogous to (42), even though the degeneracy phenomenon is encountered for the inner levels at earlier stages of approximation than for the outer ones. The reason for these statements is that the sigma doubling does not usually appreciably affect the frequencies in the denominator, and a sum of the form $\sum_k a(nk)b(km)$ over a set of degenerate levels k is invariant under a transformation T wholly within the set provided n, m do not belong to the set. (To prove the latter proposition we need only note that $a(nk)=(Ta_0T^{-1})(nk)$ reduces to $(a_0T^{-1})(nk)$ and $b(km)$ to $(Tb_0)(km)$ if m, n are not in the set k undergoing transformation. The desired invariance is then a consequence of $T^{-1}T=1$.)

where the superscript ^{z} is an abbreviation for $2\sigma-1$ primes. Here and henceforth we suppress the index j which is involved in all the elements but which remains constant as they are diagonal in j.

At this stage we must use the perturbation theory for degenerate systems. We need consider only the interaction between a pair of states $n\sigma v$ and $n-\sigma v$, as the interaction of this pair with states outside this pair gives only non-degenerate elements and a contribution to the energy of the order $B^{2\sigma+1}$. Thus the term $W^{(2\sigma)}$ of order $B^{(2\sigma)}$ in the energy is a root of the determinant

$$\begin{vmatrix} H^{(2\sigma)}(n\sigma v\,;\,n\sigma v)-W^{(2\sigma)} & H^{(2\sigma)}(n\sigma v\,;\,n-\sigma v) \\ H^{(2\sigma)}(n-\sigma v\,;\,n\sigma v) & H^{(2\sigma)}(n-\sigma v\,;\,n-\sigma v)-W^{(2\sigma)} \end{vmatrix}=0 \qquad (39)$$

Now

$$H^{(2\sigma)}(n\sigma v\,;\,n\sigma v)=H^{(2\sigma)}(n-\sigma v\,;\,n-\sigma v), \qquad (40)$$

as up the present stage there has been no discrimination between positive and negative values of σ, since simultaneous alteration of the sign of both the initial and final values of σ in (29) does not change the matrix elements (29) except possibly for phase factors involved in the P's. These phase factors do not affect the energy as this depends only on the absolute value of the matrix elements. Thus the two roots of (39) differ from each other by an amount

$$h\Delta\nu=2\left[H^{(2\sigma)}(n\sigma v\,;\,n-\sigma v)H^{(2\sigma)}(n-\sigma v\,;\,n\sigma v)\right]^{1/2}=2\left|\,H^{(2\sigma)}(n\sigma v\,;\,n-\sigma v)\,\right| \qquad (41)$$

Eq. (41) shows that the interaction between positive and negative values of σ causes a cleavage of pairs of energy levels which would otherwise coincide. This is the phenomenon of "sigma-type doubling." The width of a doublet is given by (41) to terms of lowest non-vanishing order in B, and the doubling is thus an effect of order $B^{2\sigma}$, as previously found by Kronig.[6] Hence the doubling should be much narrower for D or F than for P terms. In fact only in P terms is it ordinarily discernible. Obviously S states should show no doubling, as with $\sigma=0$ there can be no question of resonance between positive and negative values of σ.

The transformation connected with the determinant (39) "scrambles together" the angular momentum values $+\sigma$ and $-\sigma$, so that it is incorrect to identify one component of a sigma-type doublet with an angular momentum $+\sigma$ about the axis of figure, and the other component with an angular momentum $-\sigma$. Instead in either component this angular momentum continually changes sign, and has the average value zero, but its square is always approximately σ^2. The mathematical basis for these statements is that owing to (40) the transformation matrix[30] associated with (39) has the elements

$$S^{(2\sigma)}(n\sigma v\,;\,n\sigma v)=S^{(2\sigma)}(n-\sigma v\,;\,n-\sigma v)=S^{(2\sigma)}(n\sigma v\,;\,n-\sigma v)$$
$$=-S^{(2\sigma)}(n-\sigma v\,;\,n\sigma v)=(1/2)^{1/2} \qquad (42)$$

The transformation given by (42) is superposed on the transformation $S=1+S_1+S_2+\cdots$ introduced in the first $2\sigma-1$ orders of approximation made prior to the encountering of the degeneracy. However S_1, S_2, $\cdots$ $S_{2\sigma-1}$ become infinitesimal when B does, whereas the elements (42) retain finite values. The new wave functions $\Psi^0{}_{n\sigma v}=\sum_{n'\sigma'v'} S(n'\sigma'v';\ n\sigma v)\Psi^0{}_{n'\sigma'v'}$ are thus approximately $(\Psi^0{}_{n\sigma v}\pm\Psi^0{}_{n-\sigma v})/2^{1/2}$, i.e. linear combinations of the wave functions corresponding originally to left and right-handed rotations about the axis of figure. These sum and difference combinations are precisely those used by Kronig as the starting point of his perturbation calculation.

^1P states. An explicit formula for the diagonal elements of H in (39) would be exceedingly cumbersome with arbitrary values of σ, far more so than the expression (39) already derived for the off-diagonal elements. The primary interest is in the doublet widths rather than the absolute value of the energy, and (41) shows that fortunately this width does not involve the calculation of such diagonal elements. In ^1P states, however, σ equals unity, and the sigma doubling effect appears in the second approximation in B. Here it is easy to calculate the absolute as well as relative energies, for the well-known expression[30] for W_2 in non-degenerate systems[38] shows that now the diagonal elements of (39) become

$$H^{(2)}(n1v\ ;\ n1v)=H^{(2)}(n,-1v\ ;\ n,-1v)$$
$$=\sum_{n'\sigma'v'}\{\,|\,H_1(n1v\ ;\ n'\sigma'v')\,|^2/h\nu(n1v\ ;\ n'\sigma'v')\} \quad (43)$$

where $\sigma'=0,2$. Using (28), (38) and (42), we see that the roots of the determinant (39) are now

$$W^{(2\sigma)}=-2C+(C+C_1)j(j+1)\quad,\qquad -2C+(C+C_2)j(j+1) \quad (44)$$

with

$$C=4\sum_{n'v'}\frac{|\,(BP_y)(n1v\ ;\ n'2v')\,|^2}{h\nu(n1v\ ;\ n'2v')},\quad C_1=8\sum_{n'v',\text{even}S}\frac{(BP_y)(n1v\ ;\ n'0v')^2}{h\nu(n1v\ ;\ n'0v')} \quad (45)$$

where the summation over the S states $n'0$ is to be extended over only those of the even type. The expression for C_2 is similar except that the summation is over the odd S states. We classify an S state as "even" or "odd" according as its internal wave function Φ_{nov} is invariant or changes sign when one makes the transformation $x_i=x_i$, $y_i=-y_i$, $z_i=z_i$ $(i=1,\cdots f)$. This division of S levels into two types is suggested by Kronig's papers.[6] He shows that all S wave functions have either the even or odd property, as otherwise there would be two independent wave functions belonging to a single S state. Before making the tranformation (42), we can without loss

[38] Because of the degeneracy encountered in the second approximation, the expression W_2 calculated on the assumption of a non-degenerate system is not the actual second order energy, but does equal the diagonal elements of H in (39).

of generality suppose that $\Psi_{n\sigma}(x, y, z)=\Psi_{n,-\sigma}(x,-y,z)$ as in the beginning we supposed that the states $+\sigma$ and $-\sigma$ differed only in the sense of rotation about the axis of figure. The operator $l_y=i^{-1}\sum(z_i\partial\cdot\cdot/\partial x_i-x_i\partial\cdot\cdot/\partial z_i)$ is invariant with respect to the transformation under consideration. Furthermore in singlet spectra $P=l$, and hence (19) shows that P_y $(n'0;$ $n,-1)$ has the same or the opposite sign from $P_y(n'0;\ n1)$ according as the state $n'0$ is even or odd. This, taken with the Hermitian property (28) of the matrices, shows that each term in the sum (38) is real, and that (44–45) do indeed follow from (38, 39, 43). In certain simple systems it may happen that S states are all of the even type, making $C_2=0$, though this is not true in the general case. In a molecule with one electron, for instance, the S wave functions are all even, as they are of the form $\Psi_{n0}(\rho, z)$, where ρ, z are cylindrical coordinates (cf. footnote 21).

The important thing to note about Eq. (44) is that it shows that the width of a ^1P sigma-type doublet is $(C_1-C_2)j(j+1)$, and therefore approximately propotional to j.[2] Also when (44) is added to the original energy values associated with (14–16) to obtain the complete energy, we see that the inclusion of the terms in B does not impair the ability to represent the dependence of the energy on j in a rigid molecule by an expression of the form $A'+B'j(j+1)$, but the constant B', and hence the "apparent moment of inertia" computed therefrom, will have different values in the two doublet components.

If the vibrational excitation is small in the state n, though not necessarily in the state n', the formulas (45) may be simplified by the use of (23–4). Then[39]

$$\sum_{n'\sigma'v'}|\ (BP_y)(n\sigma v\ ;\ n'\sigma'v')\ |^2=B^2\sum_{n'\sigma'}|\ P_y(n\sigma\ ;\ n'\sigma')\ |^2$$

and the summation over v' in (44) can be eliminated, as ordinarily the dependence of ν on v' can be neglected in comparison with its dependence on n'. Still further simplification of (45) can be effected if we assume that the orbital angular momentum has a constant magnitude and precesses uniformly about the axis of figure, and that further the moment of inertia is independent of σ. These assumptions we will henceforth for brevity refer

[39] It is to be clearly understood that without the simplification resulting from (23–24) the matrix (BP_y) is not identical with the product of the ordinary band spectrum constant $B=h^2/8\pi^2I$ and the angular momentum matrix P_y, but is rather the product of the two matrices $B=h^2/8\pi^2Mr^2$ and P_y. The expression for (BP_y) is given by (21) and of course involves the initial and final states symmetrically. Similarly in the matrix Al, used in later sections, beginning with Eq. (54), A is not a constant but rather a matrix proportional approximately to $1/r^3$, as the magnetic coupling energy is proportional to this power of r in atoms. Simplification by means of (23–24) is necessary before A can be identified with the ordinary constant of proportionality in the multiplet width. In section 3, however, A could be considered as a constant in (33) etc. as we did not there consider the interaction of the given P spin doublet with any other electronic states; this amounts to taking diagonal terms in the matrix A. The expressions A_S, B_P, etc. to be used in section 5 starting with Eq. (58) denote the diagonal elements of A or B for an S or P state.

to as the *hypothesis of pure precession*. They are not good approximations except when the valence electron (or electrons) is in such a large orbit that it exerts little bonding power in holding the nuclei together. However, the hypothesis of pure precession is convenient and justifiable at least in estimating the order of magnitude of the $C's$. When it is made the components of l are diagonal in n, and given by expressions identical with (30) except that l, σ_l replace s, σ_s. We then find.[40]

$$C=B^2(l^2+l-2)/h\nu(1,2), \qquad C_1=2B^2l(l+1)/h\nu(1,0), \qquad C_2=0 \quad (46)$$

If we further suppose $l=1$, and that in a stationary molecule $W(\sigma)=A\sigma^2$ (i.e. that the coupling of l to the axis of figure is proportional to the square of the cosine between l and this axis) we have a model so simplified that it is the same as that used in Hill and V. V.'s[5] section on sigma-doubling, which employed a different method using Hund's case (d) (loose coupling of l relative to the rest of the molecule) rather than case (a) as the unperturbed system. Eqs. (44–45) are then identical with their corresponding formula (third line of their Eq. 43). Incidently, with these final simplifications a closed formula (2nd and 3rd lines of Hill's and V. V.'s Eq. 42) can be obtained with either method, including all powers in B, instead of using successive approximations as we do and stopping with B^2.

D states. Here by (29), (38) and (40), the dependence of the doublet separation on j is of the form

$$h\Delta\nu=d(j-1)j(j+1)(j+2) \quad (47)$$

as already mentioned by Kronig.[6] The constant d is of the order B^4 and with the hypothesis of pure precession

$$d=2B^4(l-1)l(l+1)(l+2)/h^2\nu(2,1)^2h\nu(2,0)$$

5. Sigma Doubling in ^2P States

In section 3 we considered the rotational distortion of spin multiplets, but omitted the superposed sigma-type doubling, as we disregarded the perpendicular component of orbital angular momentum. In section 4 we treated sigma-doubling without spin, which is legitimate only in singlet spectra. We must now handle the more complicated problem of the mutual interaction of the spin and sigma doubling effects. Here the latter effect does not appreciably influence the former, but the former may completely change the latter. This is true because sigma-type doublets usually have small widths compared to the separations in spin multiplets and in rotational energy sequences, and so cannot greatly modify these separations. On the other hand, the angular momentum due to spin can profoundly alter sigma doubling, so that often the latter is entirely different in ^2P states from what

[40] As the present section relates to singlet spectra, there is now no distinction between the vectors $\boldsymbol{P}$ and $\boldsymbol{l}$. Without the hypothesis of pure precession, however, the vector $\boldsymbol{l}$ does not have a constant scalar magnitude $[l(l+1)]^{1/2}$.

it is in the ^1P. In general the behavior is quite distinct depending on whether we have Hund's case (b) or (a).

Case (b). In Hund's ideal case (b) the only effect of the spin is to cause a precession of j_k, which is the total angular momentum exclusive of spin, about the inclusive total j, but this precession is so slow as to be negligible if the spin forces are very weak. Hence with perfect case (b) the effective angular momentum is that exclusive of spin, and the interaction between orbital angular momentum and molecular rotation is identical with that in a singlet molecule of total angular momentum j_k. The sigma doubling is then the same for all components of a spin multiplet, and identical in magnitude with that calculated for singlet states except that j_k everywhere replaces j. These results hold for any multiplicity. In particular we see, using (44), that in case (b) P states, the various spin components having the same value of j_k should exhibit equal sigma doublings proportional to $j_k(j_k+1)$.

Complications in case (a). As the phenomena in Hund's case (a) are more complex, we shall in the balance of this section confine our attention to ^2P levels, as they are the simplest multiplets and probably the commonest. In view of the perturbation theory given in section 4 it doubtless at first thought appears as though the $^2P_{1/2}$ component($\sigma_s=-1/2$, $\sigma=\sigma_l+\sigma_s=1/2$) should exhibit a sigma doubling width of the first order in B, and the $^2P_{3/2}$ component ($\sigma_s=1/2$, $\sigma=3/2$) one of the third order, as one transition of the type $\Delta\sigma=\pm1$ involved in the perturbing matrix elements (29) suffices to connect the states $\sigma=1/2$ and $\sigma=-1/2$ whereas the superposition of three such transitions is needed to connect $+3/2$ and $-3/2$. This, however, overlooks the fact that with the spin the criterion for terms with sigma-type degeneracy is not just $\sigma=-\sigma'$ but is instead is the more strigent condition $\sigma_s=-\sigma_s'$ $\sigma_l=-\sigma_l'$. If we neglect all interaction between the components of s and l perpendicular to the axis of figure, the spin and orbital angular momenta will precess about this axis at different, uncoordinated rates, so that the matrix elements of l_y will be all of the form $\Delta\sigma_l=\pm1$, $\Delta\sigma_s=0$, whereas those of s_y will all have $\Delta\sigma_l=0$, $\Delta\sigma_s=\pm1$. As $P_y=s_y+l_y$ the perturbing matrix elements of (29) become entirely of the forms

$$\Delta\sigma_l=\pm1,\ \Delta\sigma_s=0 \text{ and } \Delta\sigma_l=0,\ \Delta\sigma_s=\pm1 \tag{48}$$

Three transitions of this character are needed to connect $\sigma_s=-1/2$, $\sigma_l=+1$ with $\sigma_s=+1/2$, $\sigma_l=-1$ and so without interaction between the perpendicular component of s and that of l we would obtain a doubling for the $^2P_{1/2}$ component of only the third order in B, the same as for $^2P_{3/2}$. This is contrary to the experimental fact that the $^2P_{1/2}$ state often shows a much larger sigma doubling than the $^2P_{3/2}$. The reason for this observed dissymmetry is that actually there is always interaction between the components of s and l which are perpendicular to the figure axis. This can be seen in the following way:

Digression on Hund's case (c). Suppose the interaction between s and l were so large as to overpower the "non-centralness" defined in the introduction, but that the effect of non-centralness is still large compared to the

rotational distortion. We then have a situation which Hund[3] dubs case (c). The parallel components of s and l will cease to be separate quantum numbers, but the sum of these components will still have a constant quantized value σ, and the vector resultant of s and l will have a quantized magnitude i analogous to the usual inner quantum number. We use the notation i in place of Hund's j, as we reserve j for the total molecular angular momentum. If i executes a pure precession about the axis of figure, the elements (29) become of the type $\Delta i=0$, $\Delta\sigma=\pm 1$ the complication of the separate parallel quantizations σ_l and σ_s now disappearing. Sigma-type doubling is encountered when $i=i'$, $\sigma=-\sigma'$. Consequently the state $\sigma=1/2$ should exhibit a sigma doubling width of the first order in B, and proportional $j+1/2$, but the state $\sigma=3/2$ one of the third order, and proportional to$(j-1/2)(j+1/2)(j+3/2)$, as can be seen by using Eqs. (29), (38), (41). Explicit formulas for the factors of proportionally could immediately be written down, but we shall not give them, as such strong interaction between s and l as to give case (c) is a rare, if not purely academic occurrence, and as formulas for illustrative special cases of (c) have already been given by Hill and V. V. in their Eq. (43). They used another method of calculation already described, and computed the doublet widths on the assumption of a binding force proportional to $\cos^2(i,\sigma)$, with $i=1/2, 3/2$ (k in their notation), the values to be expected as the resultant of $s=1/2$ and $l=1$. The important thing to note is that the component $\sigma=1/2$ exhibits an enormous sigma doubling of the same order of magnitude as the rotational energy intervals themselves.

Actual case (a). Ordinarily Hund's case (a) represents the true state of affairs much more accurately than his case (c), but any interaction between the perpendicular component of s and that of l may be regarded as at least the beginning of a transition from case (a) to (c). Hence we can understand qualitatively why the $P_{1/2}$ state should exhibit a larger doubling than the $P_{3/2}$. Quantitatively this is due to the fact that owing to the interaction between the perpendicular component of s and that of l the matrix P_y will indeed have elements, though small, of the form $\Delta\sigma_s=+1$, $\Delta\sigma_l=-2$ which connect $\sigma_s=-1/2$, $\sigma_l=1$ and $\sigma_s=1/2$, $\sigma_l=-1$ in one transition $\Delta\sigma=-1$. The magnitude of these elements is calculated in a following paragraph and proves to be proportional to the product of B and the magnetic interaction energy, making the sigma doubling of the $P_{1/2}$ state not exceedingly large even though of the first order in B. By (29) and (41) the formula for the width of this doublet is

$$P_{1/2}) \qquad h\Delta\nu=a(j+1/2) \qquad \text{with} \qquad a=4\left|(BP_y)(P_{1/2}\,;P_{-1/2})\right| \tag{49}$$

The corresponding width for the $P_{3/2}$ state may be calculated neglecting entirely the interaction between s and l, as here unlike in $P_{1/2}$, this interaction does not make the doubling of lower order in B. This width is by (29), (38), and (41)

$$P_{3/2}) \qquad h\Delta\nu=b(j-1/2)(j+1/2)(j+3/2) \tag{50}$$

If we make the hypothesis of pure precession (p. 489) for s, but not necessarily for l, the value of the constant b is by (30)

$$b=16B\sum_S[(-1)^S\,|\,(BP_y)(P\,;S)\,|^2/h\nu(P\,;S)h\nu(P_{3/2}\,;P_{1/2})] \tag{51}$$

In writing (49), (51), and all future equations, we for brevity index the matrix elements with respect to the spectroscopic nomenclature of the initial and final states, instead of the quantum number, as indicated in the following scheme

$$\begin{gathered} {}^{S_{1/2}} \\ n,\sigma_l,\sigma_s,v=n',0,\tfrac{1}{2},v'\,; \\ {}^{S_{-1/2}} \qquad {}^{P_{3/2}} \qquad {}^{P_{1/2}} \qquad {}^{P_{-1/2}} \qquad {}^{P_{-3/2}} \\ n',0,-\tfrac{1}{2},v', \quad n',1,\tfrac{1}{2},v', \quad n',1,-\tfrac{1}{2},v', \quad n',-1,\tfrac{1}{2},v', \quad n',-1,-\tfrac{1}{2},v' \end{gathered} \tag{52}$$

Otherwise it would be necessary to list four initial and four final indices, since we must now specify σ_s in addition to the quantum numbers n, σ, v used as indices in section 4. The distinction between positive and negative subscripts, we may caution, has no direct meaning in terms of observed spectroscopic levels, but is only associated with the quantization at the outset of the calculation. Actually the sigma doubling finally scrambles together the positive and negative values, the really vital type of classification being with respect to Kronig's[6] symmetry and antisymmetry. The summation over S is to be understood to extend over both all vibrational quantum numbers v' and all electronic quantum numbers n' giving rise to S states. The omission of subscripts from the arguments as in (51) means that the spin does not appreciably influence the amplitude or frequency under consideration. In writing (51) we have neglected terms with two PS frequencies in the denominator and have utilized the fact that

$$(Bl_y)(P_+\,;S)(Bl_y)(S\,;P_-)=(-1)^S\,|\,(Bl_y)(P\,;S)\,|^2 \tag{53}$$

where the exponent S of -1 is to be taken as an odd or even integer according as the S state is odd or even in the sense explained just below Eq. (45).

Calculation of (BP_y) $(P_{1/2};\,P_{-1/2})$. This calculation is needed to estimate the order of magnitude of the constant a in (49) and may be made by perturbation theory assuming that the "magnetic" interaction energy between s and l is small compared to the effect of non-centralness. Let us further suppose that this interaction obeys the cosine law. The interaction between the components of s and l which are parallel to the figure axis merely contributes a constant term (33) in the energy which has already been utilized in section 3, and which gives the bulk of the energetic effect of the coupling between s and l. The contribution of the perpendicular components vanishes as a first approximation on averaging over the electronic frequencies, and so is a higher effect which may be considered as introducing a perturbation matrix[39]

$$H_{\text{per}}=A\,[\mathbf{s}\cdot\mathbf{l}-s_zl_z]=A\,[s_xl_x+s_yl_y] \tag{54}$$

This is, of course, not to be confused with the other perturbation matrix (29) giving the effect of rotation. As there is hitherto no coupling except through the parallel components, we can apply the phase relations (20) to s and l separately instead of to P and furthermore take the elements of l_x or l_y to be entirely of the first form (48) and those of s_x, s_y to be entirely of the second form. Hence by (20) and (48) the elements of (54) are all of the form $\Delta\sigma=0$, as we should expect. The transformation matrix corresponding to (52) is $1+S_1+\cdots$ with

$$S_1(P_{\pm 1/2}\,;S_{\pm 1/2})=2(As_yl_y)(P_{\pm 1/2}\,;S_{\pm 1/2})/h\nu(P\,;S) \tag{55}$$

The transformed matrices for BP which are corrected for the perturbing effect of (54) are given by $SB^0P_y{}^0S^{-1}=B^0P_y{}^0+S_1B^0P_y{}^0-B^0P_y{}^0S_1{}^0+\cdots$, and no longer retain the form (48). Instead we find

$$(BP_y)(P_{1/2}\,;P_{-1/2})=\text{r.p. of } 2\sum[(-1)^S(Al_y)(P\,;S)(Bl_y)(S\,;P)/h\nu(P\,;S)] \tag{56}$$

where we do not bother to attach zero superscripts to the right hand elements. We have used the Hermitian property (26), and (53) which applies to A as well as B, and use r. p. to denote the real part in case the amplitudes are complex. If the vibrational excitation of the given P state and the effect of vibration on the energy are small, the vibrational quantum number implicitly involved in the sum in (56) (cf. Eq. 52) can be eliminated by using considerations analogous to those involved in (23–24). In writing (56) we have employed simplifications which result from applying the hypothesis of pure precession to the motion of s, permitting us to use (30) with $s=1/2$. We are usually well justified in applying this hypothesis to s but not to l. If, nevertheless, we do apply it to l, we have a rough simple formula which is very convenient for estimating orders of magnitudes, etc., as then the right side of (56) reduces to a single term and the constant a in (49) thus becomes

$$a=2AB[l(l+1)]/h\nu(P\,;S). \tag{57}$$

At this point we must note that in discarding the periodic part of (13), in particular the first term of (13) in our work in section 2, we have (since $P_y=l_y+s_y$) omitted a term of precisely the same form as (54) except that A is replaced by $2B$. This neglected term ought really to be included, and has the effect of replacing A in (54–56) by $A+2B$. This modification could be neglected in the preceding study of case (a), where B/A is small by hypothesis, but is vital for the forthcoming work where we consider the entire range from (a) to (b), as otherwise the formulas do not have the proper limiting values for case (b).[41]

[41] This contribution from (13) introduces an interaction between the components of s and l which are perpendicular to the figure axis even without the supposition of magnetic forces, and shows that even without such forces the $^2P_{1/2}$ component should show a sigma doubling without going to the third approximation in B as stated on p. 490. This is a purely academic point, as by definition there is always a strong magnetic interaction in case (a). In writing

General case intermediate between (a) and (b). In treating this more complicated intermediate case, where the magnetic and rotational energies are comparable, we shall first consider the interaction between the P levels under discussion and only one particular electronic S state. The results of the interaction with the others can later be obtained by summing over all values of the electronic quantum numbers which yield S states. This procedure neglects entirely the influence of the D states, but they have only a negligible influence on the rotational distortion and sigma doubling phenomena of the P levels. With this restriction to one electronic S state, which of course has two spin components we must consider the mutual perturbation of the six levels (52). Assuming as a starting point ideal case (a) quantization as in section 3, we find that the matrix elements in the Hamiltonian connected with these six levels are as follows

$$\begin{aligned}
&H(S_{1/2}\,;\,S_{1/2})=H(S_{-1/2}\,;\,S_{-1/2})=B_S\left[j(j+1)+\tfrac{1}{4}\right]+E=\alpha\\
&H(P_{1/2}\,;\,P_{1/2})=H(P_{-1/2}\,;\,P_{-1/2})=B_P\left[j(j+1)+\tfrac{1}{4}\right]-\tfrac{1}{2}A_P=\beta\\
&H(P_{3/2}\,;\,P_{3/2})=H(P_{-3/2}\,;\,P_{-3/2})=B_P\left[j(j+1)-7/4\right]+\tfrac{1}{2}A_P=\gamma\\
&H(S_{1/2}\,;\,S_{-1/2})=H(S_{-1/2}\,;\,S_{1/2})=B_S(j+\tfrac{1}{2})=(-1)^S\delta\\
&H(P_{3/2}\,;\,P_{1/2})=H(P_{-3/2}\,;\,P_{-1/2})=B_P\left[(j-\tfrac{1}{2})(j+\tfrac{3}{2})\right]^{1/2}=\epsilon\\
&H(P_{1/2}\,;\,S_{-1/2})=(-1)^SH(P_{-1/2}\,;\,S_{1/2})=2(Bl_y)(P\,;\,S)(j+\tfrac{1}{2})=(-1)^S\zeta\\
&H(P_{3/2}\,;\,S_{1/2})=(-1)^SH(P_{-3/2}\,;\,S_{-1/2})=2(Bl_y)(P\,;\,S)\left[(j-\tfrac{1}{2})(j+\tfrac{3}{2})\right]^{1/2}=\eta\\
&H(P_{1/2}\,;\,S_{1/2})=(-1)^SH(P_{-1/2}\,;\,S_{-1/2})=(Al_y+2Bl_y)(P\,;\,S)=\theta.
\end{aligned}\tag{58}$$

Here, as elsewhere, the exponent ^{S} of -1 is to be taken as an even or odd integer, according as the S state under consideration is "even" or "odd" in the sense explained on p. 487. For convenience of later reference the various matrix elements have been designed by Greek letters, with the sign conventions which subsequently prove most convenient. The P state is taken as the origin for measuring internal electronic (or more precisely internal electronic plus vibrational) energy, so that this part of the energy will have a value $E=h\nu(P;\,S)$ different from zero, either positive or negative, often the latter, in the S state. With this observation the values given in (58) for the diagonal elements α, β, γ follow from (32–33). The values of the purely spin elements δ, ϵ follow from (29–30) or (31), and of the purely orbital elements ζ, η from (29). We suppose the magnetic interaction between the components of s and l perpendicular to the figure axis not incorporated in the unperturbed or diagonal part of the energy, as this has permitted us to calculate the other matrix elements as though the motion of s and l were completely independent, rather than perturbed by the transformation (55), a considerable simplification. Instead this interaction, when supplemented

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(58), etc., we have not included explicitly the part $B(l_x^2+l_y^2)$ coming also from the first term in (13), as this merely has the effect of altering slightly the "electronic" energy levels, and is incorporated by altering slightly the energy difference E of the S and P states.

by the correction explained in the preceding paragraph, gives rise to the matrix element θ. The specific value given for θ follows from (54) with this modification, and the assumption that the motion of s satisfies the hypothesis (30) of pure precession, but that the motion of l conforms only to the type form (20).

The secular determinant analogous to (35) for the matrix elements (58) connecting the six levels (52) could immediately be set up, and would at first appearance yield a sixth order algebraic equation for W. This equation, however, factors into two cubics because of the possibility of separating energy levels into the symmetric and antisymmetric types introduced by Kronig.[6] This separation is accomplished by introducing the following transformation matrix S

$$S(X_q\,;\,X_q)=(-1)^X S(X_q\,;\,X_{-q})=(-1)^X S(X_{-q}\,;\,X_{-q})$$
$$=-S(X_{-q}\,;\,X_q)=(1/2)^{1/2}$$

where $X=P$ or S, and where $q=-1/2$ or $1/2$, and also $-3/2$ or $3/2$ if $X=P$. The exponent X of -1 is an even integer if X represents any P state or an "even" S state, and is an odd integer if X represents an "odd" S state. As explained in connection with the somewhat similar transformation (42) this transformation is tantamount to using wave functions of Kronig's symmetric and antisymmetric types rather than those with exponential factors representing angular momentum of constant sign about the axis of figure. After the transformation the secular determinant factors into two third order determinants one of which is

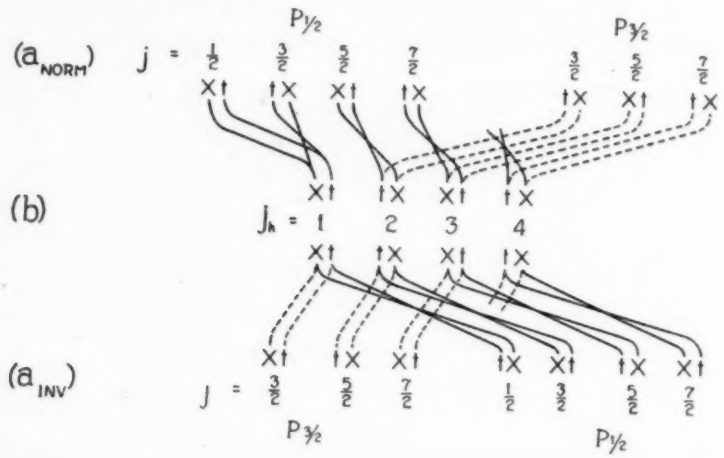
$$\begin{vmatrix} \kappa-W & \mu & \eta \\ \mu^* & \beta-W & \epsilon \\ \eta^* & \epsilon^* & \gamma-W \end{vmatrix}=0 \tag{59}$$

with $\kappa=\alpha+\delta$, $\mu=\theta+\zeta$. The other is identical except that it has $\kappa=\alpha-\delta$, $\mu=\theta-\zeta$. As a check on the work, it may be verified that when the magnetic interaction is zero, making $A=0$ in (58) these two cubics each factor into a quadratic and linear equation as follows:

$$\{[E+B_S j_{k_1}(j_{k_1}+1)-W][B_P j_{k_1}(j_{k_1}+1)-B_P-W]$$
$$-8\,|\,(Bl_y)(P\,;\,S)\,|^2\,j_{k_1}(j_{k_1}+1)\}\times\{B_P j_{k_2}(j_{k_2}+1)-B_P-W\}=0 \tag{60}$$

with $j_{k_1}=j\pm 1/2(-1)^S$, $j_{k_2}=j\mp 1/2(-1)^S$. The equations for W furnished by (60) are exactly those which would have been obtained by neglecting spin, as we should expect for the limiting case (b). Such equations for W neglecting spin have not previously been given explicitly, but are obtained by considerations closely related to those in our derivation of (44), the difference being that the interaction with one S state is treated in an exact secular fashion rather than that with all states by methods of successive approximations. The behavior (60) furnishes the clue to the adiabatic

correlation of energy levels in cases (a) and (b), which is indicated schematically in the following diagram:



The symbols × and † represent states having the two different types of Kronig[6] symmetry. These diagrams may be regarded as supplementing the previous derivation of the correlation given by Hill and V. V.[5] which did not include the sigma doubling phenomenon but to which the reader is referred for discussion and references exclusive of it. If the interaction with the spin is supposed to completely disappear in case (b) the two components of the spin multiplet coalesce in energy, as indicated by the coming together of the heavy and dashed lines corresponding to $P_{1/2}$ and $P_{3/2}$ levels respectively. It is to be noted that in the $P_{1/2}$ levels the two sigma doublet components representing different symmetries "cross over" in going from (a) to (b) except the anomalous component $j=1/2$ in regular multiplets. This means that for any particular $j>1/2$ there is an appropriate value of the ratio of rotational to magnetic energy which makes the $P_{1/2}$ sigma doubling vanish. The so-called "non-crossing" rule does not apply to these components, as they do not "combine" in the energy or secular determinant although they do spectroscopically. As shown by Kronig, the only spectral lines which are "allowed" are those which connect levels × and † with opposite types of symmetry.[42] This rule is clearly to be distinguished from the fact that in the Hamiltonian or secular determinant the only non-vanishing matrix elements are those connecting states of similar symmetry. The reason for this difference is that the energy terms are symmetrical, the electrical moment antisymmetrical as regards Kronig's transformation (15).

Ordinarily the difference in energy between the S and P state is large compared to the width of the spin doublet. If this is true, as we assume throughout, and if we are interested only in the roots corresponding to P levels, we can to a good approximation set $\kappa - W$ equal to a constant $-h\nu$

[42] Our symbols are essentially similar to those of Wigner and Witmer, and are not the same as the system used in Kronig's first paper and a preceding one by Hulthén.

(P, S) in the determinant (59), which then yields a quadratic equation for W. If we neglect terms above the first order in $1/h\nu(P; S)$, which incidentally is required to make the approximation legitimate, the solution for W is then

$$2W=\beta+\gamma\pm B_P X+\{1/h\nu(P\,;S)\}\{\mu\mu^*+\eta\eta^* \pm B_P{}^{-1}X^{-1}[(\beta-\gamma)(\mu\mu^*-\eta\eta^*)+2\mu\epsilon\eta^*+2\mu^*\epsilon^*\eta]\} \quad (61)$$

with

$$X^2=[(\beta-\gamma)^2+4\epsilon\epsilon^*]/B_P{}^2=[\lambda(\lambda-4)+4(j+\tfrac{1}{2})^2], \quad \lambda=A_P/B_P \quad (62)$$

The first three right hand terms give Hill and V. V.'s formula, our (36), for the rotational distortion of a spin doublet. The remaining terms are corrections for the influence of the S state, whose most interesting effect is the introduction of sigma-type doubling. The two values of the sign before the radical X give rise to the two components of a spin multiplet, while a sigma-type doublet is generated by giving μ the two values $\theta+\zeta$ and $\theta-\zeta$ in (61). A more explicit formula for the sigma doublet width can be obtained by substituting detailed formulas (58) for the various Greek letters. At the same time we shall sum over all the electronic S states, so that we include the interaction with all rather than one of them. We thus find

$$h\Delta\nu=\text{r.p. of } 4(j+\tfrac{1}{2})\sum_S[(-1)^S/h\nu(P\,;S)] \cdot[(2Bl_y+Al_y)(P\,;S)(Bl_y)(S\,;P)(1\pm 2X^{-1}\mp\lambda X^{-1}) \pm 4X^{-1}(j+\tfrac{3}{2})(j-\tfrac{1}{2})\,|\,(Bl_y)(P\,;S)\,|^2] \quad (63)$$

where X is as in (62) and the convention on the exponent S is as previously. The upper sign gives the $P_{1/2}$ state and the lower the $P_{3/2}$ or vice versa. It is readily verified that (63) reduces to (44–45) in the limiting case (b) and to (49–50) supplemented by (56) and (51) in the limiting case (a). Instead of first introducing a cubic secular determinant and then later summing over all the S states, Eq. (63) could also have been obtained by first applying Hill and V. V.'s transformation T to take into account the rotational distortion of the spin in which only the parallel component of s is considered, and then applying perturbation theory as in section 3 to take into account the sigma doubling phenomena, where the perpendicular components are vital. It is, however, probably more vivid to first reduce the problem to a simple algebraic equation rather than to apply the rather abstract perturbation theory at the outset.

6. Rho-type Doubling in ^2S states

In ^2S states the magnetic interaction is, of course, so weak that Hund's case (b) is a good approximation. The usual procedure is to neglect entirely the interaction between the spin and the rest of the molecule in such states, as a stationary molecule in an S level has no orbital angular momentum parallel to the axis of figure. The energy is then a function of j_k but not of j,

and there are two states of coincident energy corresponding to the possibilities $j=j_k\pm 1/2$. Actually these two S states of similar j_k but unlike j do not coincide but form a closely spaced "ρ-type doublet" in Mulliken's terminology.[43] The reason for this nomenclature is that the S rotational energy levels can be represented empirically by a formula of the type $B_S(j\pm\rho)^2$ where ρ is not exactly $1/2$, making the doublet width

$$h\Delta\nu=B_S[(j_k-\tfrac{1}{2}+\rho)^2-(j_k+\tfrac{1}{2}-\rho)^2]=2j_kB_S(2\rho-1) \tag{64}$$

A rho-type doublet is not to be confused with the sigma-type doublets found in ^2P states, as in the latter both components have the same j values rather than values differing by one unit.

A theoretical explanation of the rho-type doubling may be found in the fact that even in S states the mean square of the orbital angular momentum does not vanish[44] but instead there is a precessing component $(l_x^2+l_y^2)^{1/2}$ perpendicular to the axis of figure. This will exert a force on the spin angular momentum, but does not influence the energy in the first approximation, as the average value of the cosine of the angle between l_x or l_y and s is zero with ideal case (b) coupling. When, however, higher approximations involving the superposition of rotational distortion and this interaction are considered, the energy of the ^2S state depends on j as well as j_k. This can be seen from the determinant(59). In the preceding section we calculated the two roots of this determinant which represent P states, and we must now compute the remaining root which is an S term and which lies close to κ. The value $W=\kappa=E+B_Sj_k(j_k+1)$ is, in fact, the usual approximate formula for ^2S levels, and is obtained by neglecting the interaction between the S and P states which is embodied by the matrix elements μ, η in (59). As we may suppose κ numerically large compared to the other Greek letters and as $\kappa-W$ is numerically small compared to $\beta-W$ and $\gamma-W$, a more accurate expression for this root may be obtained by expanding the determinant and keeping only the terms which have factors $\beta-W$ or $\gamma-W$. These two factors may be replaced by their approximate values $\beta-\kappa$ and $\gamma-\kappa$, making (59) a linear equation for W. We thus find

$$W-\kappa=[\mu\mu^*/(\kappa-\beta)]+[\eta\eta^*/(\kappa-\gamma)]$$

a result also obvious from perturbation theory, as the right-hand side is essentially Born, Heisenberg, and Jordan's expression[30] for W_2. When we substitute the explicit expressions for the various Greek letters given in (58) and in the text following (59), we find that the two W's having the same j_k are

$$W=B_S'j_k(j_k+1)+E+A_S+\tfrac{1}{4}a'\pm\tfrac{1}{2}h\Delta\nu, \quad h\Delta\nu=a'(j_k+\tfrac{1}{2}) \tag{65}$$

with
$$a'=\text{r.p. of } 8\sum_P[(Al_y)(S\,;\,P)(Bl_y)(P\,;\,S)/h\nu(S\,;\,P)] \tag{66}$$

[43] R. S. Mulliken, Phys. Rev. **28**, 481 (1926).
[44] Cf. J. H. Van Vleck, Phys. Rev. **31** 600 (1928).

$$B_S' = B_S + 8\sum_P [\,|\,(Bl_y)(S\,;P)\,|^2/h\nu(S\,;P)\,],\quad A_S = \sum_P [\,|\,(Al_y)(S\,;P)\,|^2/h\nu(S\,;P)\,].$$

The two cases represented by the choice of sign correspond to $j = j_k \mp 1/2$, $\kappa = \alpha \pm (-1)^S\delta$, $\mu = \theta \pm (-1)^S\zeta$. The summation over all the electronic ^2P states is included to remove the restriction, made in deriving (59), that the given ^2S states interacts with only one ^2P spin doublet. As we should expect, the doubling phenonenon disappears and the energy becomes a function only of j_k when the magnetic interaction is disregarded by setting $A = 0$.

The variation of the rho-doublet width with j_k given by (65) is precisely that found by Mulliken except for the small difference that (65) has $j_k + 1/2$ in place of j_k, a modification which is supported by more precise experimental data[45] available subsequent to Mulliken's[43] early work. The order of magnitude of the constant a' is the same as that of the constant a in the formulas (49,56) for the width of a case (a) sigma doublet. In fact the constants are identical except for sign if a ^2S state and a ^2P spin doublet be imagined to interact only with each other and not with other electronic P or S states, and if in addition B/A is negligible. With the hypothesis of pure precession, a' is the negative of the expression (57).

This explanation of rho-type doubling, which was suggested in part by a conversation by Professor Kemble, is not quite the conventional one given by Hund[3] and others.[45] The ordinary interpretion assumes that in S states the molecule develops some angular momentum due to the orbital motion of the nuclei in their rotation about the center of gravity. This angular momentum, which will have the direction of j_k, will interact with the spin angular momentum s, and the energy of this interaction may be taken to be of the form

$$a''j_k \cdot s = \tfrac{1}{2}a''[j(j+1) - j_k(j_k+1) - s(s+1)] \qquad (67)$$

where a'' is of the order m/M times the factor of proportionality A in the ordinary spin P doublets, m/M being the ratio of the electronic mass to the "reduced mass" of the nuclei. On the right-hand side of (67) we have given the value of the vector product furnished by the cosine law of quantum mechanics. The difference between the values of (67) for $j = j_k + 1/2$ and $j = j_k - 1/2$ is

$$h\Delta\nu = a''(j_k + \tfrac{1}{2}). \qquad (68)$$

The conventional explanation (67) thus gives precisely the same dependence of the rho-doubling width on j_k as our previous formulas (65–66). Actually the two effects are additive, so that the true value of the constant of proportionality in (65) or (68) should be $a' + a''$. To compare the relative importance of the two contributions, we first note that (66) and (68) give constants of proportionality respectively of the order $8B/h\nu(S, P)$ and m/M times the width of an ordinary spin doublet. Now m/M is of the order $10^{-3}/4Z$, where Z is the atomic number of the lighter of the two nuclei, while $B/h\nu$

[45] Hulthén, Zeitz. f. Physik **50**, 319 (1928).

(S, P) seems ordinarily to be about 10^{-4} (see section 8 for numerical data on ν). Consequently a' is certainly larger in magnitude than the factor a'' usually given, provided Z is large. Ostensibly because of the factor 8×10^{-4} as against $10^{-8}/4$, a' should predominate slightly over a'' even in light molecules, such as the hydrides $Z=1$, but of course much credence should not be placed on a predominance merely in virtue of such numerical factors until an accurate calculation can be made of the amount of magnetic moment developed by the nuclear orbital motions or until the sum in (66) can be evaluated accurately through knowledge of the ν's and the precise form of the orbital angular momentum matrix l.

Even the part of the rho-type doubling represented by (66) is due in a certain limited sense to magnetization by rotation, the cause ordinarily given, as the rotational distortion makes the component of electronic orbital angular momentum which is perpendicular to the axis of figure precess at a non-uniform rate, so that it precesses at different speeds in the configurations which are approximately parallel or antiparallel to j. A mean electronic angular momentum in the direction of j_k is thus developed, and the interaction between this and s will depend on the angle between j_k and s in the fashion (67), thus giving[46] the rho-type doubling (65–66). An analagous physical interpretation can be given the sigma-doubling (49) in case (a) $^2P^{1/2}$ states; the rotational distortion causes the perpendicular components of s and l to precess non-uniformly, so that they both slow or speed up when nearly parallel to j (Whether there is slowing or speeding up depends on the sign of the important frequencies $\nu(\mathrm{P};\mathrm{S})$.) This non-uniformity makes the mean cosine and interaction energy between these components no longer zero and removal of the degeneracy with respect to the sign of σ gives the sigma type doubling. In our treatment of ^2P states in section 5, we ought really to have included also the interaction between the electronic angular momentum, orbital and especially spin, with the magnetic moment in the

[46] This physical picture, suggested me by Kemble, of rho-type doubling as due to development of a magnetic moment by rotational distortion may appear superficially rather different from the purely mathematical way in which we extracted the formulas (65–66) from the determinant (59). That the results are the same can be seen as follows: On the basis of this physical picture the energy of magnetic interaction responsible for the rho-doubling is the expression

$$(Al\cdot j_k)(j_k\cdot s)/(j_k^2+j_k) \qquad \text{(I)}$$

The first vector product of this expression vanishes on the average if we neglect the rotational distortion and consists of the non-diagonal elements

$$(Al\cdot j_k)(\mathrm{s};\mathrm{P}_{+1})=(-1)^S(Al\cdot j_k)(\mathrm{s};\mathrm{P}_{-1})=(Al_y)(\mathrm{s};\mathrm{P})(j_k^2+j_k)^{1/2} \qquad \text{(II)}$$

We include A inside the parenthesis because, unlike the factor a'' in (67), it must be treated as a matrix rather than as an ordinary numerical factor. (cf. note 39) Formula (II) can be derived by using the same type of kinematical argument as that on pp. 257–258 of Hill and V. V. but taking the electronic angular momentum as now perpendicular rather than parallel to the axis of figure. The rotational distortion has the effect of introducing the transformation matrix (37). When this is applied to (II), the diagonal elements of the expression (II) no longer vanish. When (29) and (I–II) are treated as simultaneous perturbing functions they are found to lead to the same sigma doubling as given in (65–66).

direction of j_k or j developed by the nuclear orbital motions, but this interaction which is essentially the same as that involved in the conventional explanation of rho-type doubling, is usually masked by the other terms except possibly when considering spin doubling when very, very, close to Hund's case (b). Hence we have not complicated the formulas by its inclusion.

Fine structure of ^3S *states.* This has been treated by Kramers[47] and will not be considered. He shows that the most important term is one which results from the interaction of the two individual electron spins that compound vectorially to give $s=1$. This term is usually absent in ^2S states because they ordinarily contain only one uncompensated electron.[48] We have therefore disregarded it in discussing them. In triplet molecules, however, it introduces a coupling proportional to the square of the cosine of the angle between s and the axis of figure. Superposed on this term in ^3S states, there are the two effects responsible for the rho-doubling considered above. Kramers does not consider these effects explicitly but notes that inclusion of a term of the type form which they give does not improve the agreement with experiment in oxygen.

7. Sigma Doubling in ^3P States

Let us now revert to sigma-doubling and study case (a) ^3P states. Case (b) is, of course, trivial, as the sigma-doubling phenomena are there the same as in ^1P states except that j_k replaces j. In case (a) the $^3P_2$ component clearly exhibits a negligible sigma-doubling, as the resonance terms enter only in the fourth approximation. The $^3P_1$ state should exhibit approximately the same doubling proportional to $j(j+1)$ as a ^1P state, the reason being that in a $^3P_1$ level the spin makes no contribution to σ. The $^3P_0$ component is particularly interesting, as it splits into two sub-components even in a stationary molecule. The resulting doubling is therefore approximately independent of j, and is quite different from the ordinary sigma doubling induced by the rotational distortion. The reason for this anomalous behavior of the $^3P_1$ state is that the magnetic interaction between s and l introduces terms in the Hamiltonian of the form $\Delta\sigma=0$, and can therefore bring about a "resonance" between $+\sigma_l$, $+\sigma_s$ and $-\sigma_l$, $-\sigma_s$ if $\sigma_l+\sigma_s=\sigma=0$. On the other hand the rotational distortion terms (29) of the type $\Delta\sigma=\pm1$ are needed to introduce this resonance if $\sigma_l+\sigma_s\neq0$. That the magnetic interaction actually does split the $^3P_0$ level even in a stationary molecule can be seen qualitatively by using the same sort of argument as on p. 491. In the nomenclature there used, any magnetic interaction can be regarded as at least a slight tendency from Hund's case (a) to his case (c), and with given l and $s=1$ there are states with three values of i in case (c), viz., $i=l-1, l, l+1$ which have $\sigma=0$. When we pass over to Hund's case (a) by

[47] H. A. Kramers, Zeits. f. Physik, in press.

[48] In doublet spectra possessing inverted P states we ought perhaps to consider an effect analagous to that studied by Kramers, as such inverted spectra are characteristic of three rather than one uncompensated electron. (cf. R. S. Mulliken, Phys. Rev. **32**, 186, 1928.)

making the magnetic interaction gradually disappear, these three states go adiabatically into one $^3S_0$ and two $^3P_0$ levels, showing that a non-vanishing magnetic coupling gives two $^3P_0$ levels of different energies. The reason that these two energies are nearly the same in case (a) is that the magnetic interaction is overpowered by the non-centralness. The two $^3P_0$ levels are really part of a spin multiplet, and are respectively symmetric and antisymmetric as regards Kronig's transformation (15) generalized[9] to include the spin. In the nomenclature of Wigner and Witmer,[7] they would be classified as a 0, 0′ pair.

The magnitude of the $^3P_0$ doubling may be calculated quantitatively by using perturbation methods similar to those employed in preceding sections. We take a perturbation function of the form (54) and calculate the transformation matrix S_1, but with now $s=1$ instead of $s=1/2$ as in (55). Application of this transformation has the effect of introducing as on p. 485 a new perturbing Hamiltonian function of the second and higher orders which contains elements of the form

$$H^{(2)}(+1\ ,\ -1\ ;\ -1,+1)=2\sum_S(-1)\ [\,|\,Al_\nu(P\ ;\ S)\,|^2/h\nu(P\ ;\ S)\,] \qquad (69)$$

where the indices are σ_l and σ_s. By analogy with (39–40–41) (the difference being that the perturbations are magnetic instead of rotational), the doublet width is just twice the expression (69). In obtaining (69) we have applied the hypothesis (30) of pure precession only to s. If we apply it also to l, so as to simplify the sum in (69) then

$$h\Delta\nu=A^2l(l+1)/h\nu(P\ ;\ S)\ . \qquad (70)$$

8. Summary and Comparison With Experiment

The conclusions regarding the widths of sigma type doublets in various limiting cases are summarized in the following table:[49]

^1P	$\Delta\nu=(C_1-C_2)j(j+1)$	AlH
^2P case (b)	$\Delta\nu_{1/2}=\Delta\nu_{3/2}=(C_1-C_2)j_k(j_k+1)$	CH, OH
^2P case (a)	$\Delta\nu_{1/2}=a(j+\frac{1}{2}),\ \ \Delta\nu_{3/2}=b(j^2-\frac{1}{4})(j+\frac{3}{2})\sim 0$	HgH, CdH, ZnH, BO, NO.
^3P case (b)	$\Delta\nu_0=\Delta\nu_1=\Delta\nu_2=(C_1-C_2)j_k(j_k+1)$	C_2, He_2[50]
^3P case (a)	$\Delta\nu_0=f,\ \ \Delta\nu_1=(C_1-C_2)j(j+1),\ \ \Delta\nu_2\sim 0$	N_2
^1D or ^2D	$\Delta\nu\sim 0$	CH

^2S (rho-type doubling). $\Delta\nu=a'(j_k+\frac{1}{2})$

Here $\Delta\nu_{1/2}$ means the sigma doubling width of the $P_{1/2}$ spin component, etc. The orders of magnitudes of the constants of proportionality may be estimated on the crude assumption that the motion of l is one of pure precession (cf. p. 489) and that $l=1$. Then

$$C_1-C_2=4B^2/\nu,\quad a=-a'=4AB/\nu,\quad b=8B^3/\nu A,\quad f=2A^2/\nu \qquad (71)$$

[49] The table and Eq. (71) are derived primarily from our Eqs. (44), (46), (47), (49), (50), (57), (65), (66), and (70) and related discussion in the text.

[50] We take only the 2^3P state of He_2, as in other states the orbital angular momentum is too loosely coupled to the axis of figure, i.e. the non-centralness is too small, to permit application of the theory as we have given it. See section (e) of Mulliken's paper.

where A denotes the width of the spin doublet (or half that of the spin triplet) in wave numbers, ν is the wave number of the $P \rightarrow S$ transition, and $B = h/8\pi^2 Ic$. This is a change for reasons of numerical convenience from our previous convention in which A, B referred to measurements in ergs and ν to the frequency scale. The explicit formula (47) for the width of a ^1D sigma doublet has not been repeated, as this width is negligible; with for instance $B=5$, $\nu=10^4$, $l=2$, (47) gives $\Delta\nu \sim 10^{-8}(j^2-1)\ (j^2+2j)$ cm^{-1}. The sigma doubling for ^2D states has not been calculated in our paper, but is also clearly too small to detect, as it is easily seen to be of the third or higher order in B. In case (a) the sigma doubling of the $^2P_{3/2}$ component is likewise negligible unless j is exceedingly large;[51] $B=5$, $A=100$; $\nu=10^4$, for instance, makes the constant of porportionality b of the order 10^{-3} cm^{-1}.

A full enumeration of empirical results on sigma type doubling is given in the following paper by Mulliken, to which the reader is referred for numerical experimental results. The right hand column in our table gives the various types of molecules listed therein whose observed doubling corresponds to the predicted. In general the qualitative agreement is very satisfactory. The ^2P states are particularly interesting, as here both the theoretical predictions and experimental data are most copious. Molecules known to conform quite accurately to case (b) coupling are found experimentally to have an approximately equal doubling for both spin components, whereas those known to conform to case (a) exhibit a highly asymmetrical behavior of the two spin components, the doubling of the $P_{3/2}$ level being too small to resolve, whereas that of the $P_{1/2}$ is large and varies linearly with j. These are just the theoretical predictions. Hulthén's[45] experimental work on HgH even confirms the additive constant 1/2 in the theoretical factor $j+1/2$ for case (a) $^2P_{1/2}$ states.

To check the predicted order of magnitude for the constant a, and especially its mode of variation with A and B, one may take the observed values of A and B given by Mulliken in still another paper[52] and then determine the values of ν which make (71) yield the values of a found by Mulliken. The ν values so found are

$\nu \times 10^{-4} = 2.8$, 3.3 (HgH); 3.3 (CdH); 3.2 (ZnH); 2.7 (BO); 8.4 (NO)[53] cm^{-1}.

This approximate constancy of the calculated ν from molecule to molecule must be regarded as quite remarkable, for the corresponding variation of the constant of proportionality a measuring the amount of sigma doubling is by a factor over 100. This variation of a is due mostly to the different spin doublet widths A, which likewise vary by a factor over 100, whereas B

[51] Hulthén[45] in his Fig. 5 seems to show that there is a perceptible doubling of the $^2P_{3/2}$ level for large values of j (20 or so) as we might expect. This is not to be confused with the perturbation phenomena he finds at $j=10$. The departures from linearity which he finds for large j in the $^2P_{1/2}$ component may be the beginning of the ultimate "crossing over" for this component predicted by our figure in section 5.

[52] R. S. Mulliken, Phys. Rev. **32**, 388 (1928), especially table 2.

[53] We make this calculation only for the normal state of NO as it is still uncertain whether the experimental value of a for the upper state is .005 or .025.

varies by a factor 6 in going from BO to HgH. The HgH molecule has the widest spin multiplet, and this is reflected in its holding the record for large sigma doubling. The two values of ν given for HgH are for different vibrational states $n=0$ and $n=1$ respectively, with account taken of the different moments of inertia found by Hulthén.[45]

The orders of magnitude 3×10^4 to 10^5 obtained for ν are indeed reasonable, as they correspond to an ultra-violet region in which molecular bands are quite common; the intense HgH $^2P-{}^2S$ bands, for instance, have $\nu=3\times10^4$ cm^{-1}. It must be emphasized that there is no reason why ν should be constant in going from one molecule to another except as regards rough orders of magnitude (perhaps the nearest decimal), for different molecules have different spectroscopic frequencies, and in the rigorous theoretical formulas the crude hypothesis of pure precession ought to be replaced by a complicated summation over all S states. For the latter reason, and also because l may actually be different from the value 1 assumed for simplicity, no agreement should be expected between the above calculated ν and an actual spectroscopic one, except on the order of magnitude. The agreement found above is closer than we should have any right to expect—especially remarkable is the approximate constancy of ν from element to element, which must mean that the $^2P\rightarrow{}^2S$ transitions that are involved are "peripheral" rather than "central" molecular properties, connected with outer rather than inner electrons. Another point, not shown by the above formulas for $\Delta\nu$, in which the theory and experiment are in accord, is that the center of a case (a) sigma doublet, i.e. mean of the two levels, is unaffected by the sigma doublet correction so that it can be represented without introducing a linear term in j. (Cf. note 8 of Mulliken's paper.)

A similar procedure may be applied to ^1P or case (b) ^2P and ^3P levels, and the values of ν determined which with known B will by (71) yield the observed C_1—C_2. The results are as follows

$$\nu\times10^{-4}=0.2\ (\mathrm{AlH}\ {}^1P);2.2\ (\mathrm{CH}\ {}^2P);3.4\ (\mathrm{OH}\ {}^2P);.89\ (\mathrm{He_2}\ {}^3P):2.7\ (\mathrm{C_2}\ {}^3P)\ \mathrm{cm}^{-1}$$

The orders of magnitude are again sufficiently reasonable.[54]

The experimental data for case (a) ^3P states are rather qualitative, but give one of the most interesting confirmations of the theory. In N_2 the data quoted by Mulliken really seem to show that here the $^3P_2$ doubling is negligible, and the $^3P_0$ doubling practically independent of j, a particularly important point since the theory in section 7 indicated that the $^3P_0$ doubling should be primarily due to a magnetic action independent of the rotation j. The data indicate a detectable and smaller doubling for the $^3P_1$ state but are too qualitative to test the theoretical proportionality to $j(j+1)$, although the data for C_2 and He_2 do actually confirm the factor $j_k(j_k+1)$ in case (b). Again, we may note that for small values of j the rotational distortion is so small that C_2 comes closer to Hund's case (a) than case (b), although we have listed it (b) in the table, and it is found that the doubling for the $^3P_0$ com-

[54] CH has a ^2S level 25,700 cm^{-1} above the normal ^2P state, but the close agreement of the calculated value 22,000 with this may be only fortuitous.

ponent extrapolates for $j=0$ to the finite value .4, whereas for the $^3P_1$ and $^3P_2$ components it probably extrapolates to zero. Here also the predicted effect is thus confirmed. The data on ^3P states in case (a) are not sufficiently accurate to permit the calculation of ν values as in the other cases. The reason is that the multiplet widths are not known, and that further it has not yet been possible to resolve the contributions of the initial and final states to the observed spectral bands. (For this reason the ν value for C_2 in case (b) given in the preceding paragraph is not reliable). We must thus be content with examining whether the observed values .24 (N_2) and .4 (C_2) for the constant f are at all reasonable. If for example we set $A=100$, $\nu=2\times10^4$, Eq. (71) gives $f=1$, a value sufficiently close.

Some of the molecules (CO, H_2, CaH, MgH) in Mulliken's table have not been included in our right hand column. In CO the doubling is too small to resolve and in CaH, MgH the variation with j seems to be rather irregular, while the data for H_2 are too qualitative to be useful. The irregular variation in MgH or CaH may be due to a coupling intermediate between the limiting cases (a) and (b), where a simple behavior can no longer be expected, or more likely that for some of the j values there is a close resonance between an S and a P state, so that the frequency ν in the denominator is nearly zero instead of large as we suppose throughout.[55] In fact band spectrum analysis shows that in CaH there is a ^2S state very near the ^2P, and under these circumstances we should expect a large, irregular doubling. This is reflected in the ^2S state actually exhibiting an unusually large rho-doubling, as we should expect with the explanation of rho-doubling given in section 6 as a rotational distortion effect, but not with the older explanation as magnetization by nuclear rotation. Such a close resonance between an S and a P state gives rise to the phenomena of "perturbations" and "predissociation" which have been treated by Kronig,[6] and which we do not aim to discuss in the present paper although the mathematics is very similar to that we use. We may, however, note that this perturbation effect explains nicely why Hulthén observes a pronounced sigma doubling of the $^2P_{3/2}$ state in HgH at a certain critical j although in general the doubling in this state is inconsequential except for great j.

In case (a) the asymmetrical doubling behavior of the various components, in which the lowest value of σ gives the widest sigma doubling, furnishes a valuable criterion for determining whether a spin multiplet is "normal" or "inverted" if not known otherwise. This idea was suggested to me by Professor Mulliken. The sigma doubling shows, for instance, unequivocably that the BO spin doublet is inverted, a point not quite certain otherwise. In C_2 and N_2 it identifies the P_0-P_0 bands but does not tell whether the N_2 multiplets are regular or inverted as existing spectroscopic data does not ioslate the energy contributions of the initial and final states.

[55] These causes may explain why Mulliken finds C_1-C_2 to be 25 per cent greater for one spin component of OH than for the other. In particular there is here not ideal case (b) so that traces of case (a) dissymmetry may have begun to show.

We shall not discuss in detail the experimental confirmation of the formula for rho-type doubling, but experiment seems to confirm nicely the theoretical type of variation with j and the prediction that the constant of proportionality a' be of roughly the same magnitude as the doubling constant a for case (a) P states.[56]

The writer wishes to express his hearty thanks to Professor Mulliken for much useful information on the experimental data and to Professor Kemble for valuable suggestions on rho-type doubling.

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January 31, 1929.

[56] The experimental values of the constant a' in ^2S doublets are often very close to the constant a in the ^2P ones. (See Fig. 4 of ref. [52]) (The distinction in sign given by 71 is not detectable.) An exact equality is not to be expected, as the hypothesis of pure precession is not accurate, and also we have neglected the part of rho-type doubling due to magnetic moment developed by nuclear orbital motions, so that we ought to add in the contribution given by Eqs. (67–68). We have not included (68) in (71) as (71) aims only at orders of magnitude. However, experimental evidence for nearly equal a' and a may be taken to mean strong interaction between a given P and S state.

ELECTRONIC STATES AND BAND SPECTRUM STRUCTURE IN DIATOMIC MOLECULES. VIII. SOME EMPIRICAL RELATIONS IN σ-TYPE DOUBLING

By Robert S. Mulliken

Abstract

Some of the empirical relations which exist in σ-type doubling are summarized. In particular, the magnitudes of the doublet intervals as a function of j, and in relation to $\Delta E/B$, are considered. The observed relations, although very varied, are consistently in agreement with theoretical work of Van Vleck (cf. preceding paper). Van Vleck's work shows definitely that the ^3P levels involved in the *second positive nitrogen bands* are both normal (not inverted).

Empirical Relations. In previous papers of this series,[1] data have been accumulated on the sign[2] and magnitude of the difference $F_A(j)-F_B(j)$ in σ-type doubling. It seems appropriate now to summarize the empirical results, so that they may be more readily available for comparison with theory. This is done in Table I below.—When reference is made to previous papers of this series, they are cited by number (I, II, etc.).

The differences found empirically between corresponding $F_A(j)$ and $F_B(j)$ terms for singlet states can be expressed in the following way,[3] where $\alpha=A$ or B:

$$F_\alpha(j)=C_\alpha+B_\alpha^*[j(j+1)-\sigma^2]+c_\alpha j+\cdots \quad (1)$$

Except in the He_2 bands, where a partial uncoupling of σ from the molecular axis occurs,[4] $C_\alpha=C_\beta=C$ and $c_\alpha=0=c_\beta$.

For doublet and triplet states, the following expressions are empirically adequate provided $|\Delta E/B|$ is not too small; corresponding expressions hold (cf. Table I of VII)[1] for small values of $|\Delta E/B|$:

$$F_{i\alpha}(j)=C_{i\alpha}+B_{i\alpha}^*[j(j+1)-\sigma_i^2]+c_{i\alpha}(j+\tfrac{1}{2})+\cdots \quad (2)$$

In Eq. (2), $i=1$ or 2 for doublet states, 1, 2, or 3 for triplet states. We have already considered how $F_{i\alpha}(j)$ depends on i for doublet states (cf. VII, Tables I, II, and Fig. 1).

We are now interested in the dependence of $F_\alpha(j)$ or $F_{i\alpha}(j)$ on α. In many cases the observed differences between $F_{i\alpha}(j)$ and $F_{i\beta}(j)$ states can be expressed by assuming a difference in the B^*'s only, or in the c's only, of

[1] R. S. Mulliken, Phys. Rev. 1926–8: I–VII of this series.

[2] Probably no definite significance can be attached at present to the *sign* of F_A-F_B, since the subscripts A and B have been assigned by a method which is probably arbitrary (cf. VI, pp. 789–92). They are at any rate not to be identified with the two types of Kronig symmetry.[21]

[3] Cf. II, Eq. (3): Phys. Rev. **28,** 1207 (1926).

[4] W. Weizel, Zeits. f. Physik **52,** 175 (1928).

TABLE I. *Summary of empirical energy relations in σ-type doubling. (Note: where a specific reference is not given, the data are from VII of this series.)*

a. ^1P states.

H_2 (initial levels, Werner bands[5]):
$F_A(j)-F_B(j)$ moderately large, negative, increasing with j, varying with vibrational quantum number.

He_2 (cf. section *e*, below)

CO (final state of Angström and Thalén bands):[6]
$F_A(j)-F_B(j)\backsim 0$

AlH: $F_A(j)-F_B(j)$ negative: $B^*_A\backsim 5.935$, $B^*_B\backsim 6.00$, $c_\alpha\backsim 0$, for $n=0$.[6, 7]
F_2 : $F_A(j)-F_B(j)$ obeying Eq. (1), with $c_\alpha\backsim 0$.[4a]

b. ^2P states (cf. Table II of VII, for ΔE values). Note: $F_{1\alpha}$ states are $^2P_{1/2}$ states for normal ^2P levels (HgH, *etc.*) *and $^2P_{3/2}$ for inverted ^2P levels* (OH, BO).

Molecule	$F_{1\alpha}$ *states*	$F_{2\alpha}$ *states*
HgH	$F_{1A}(j)-F_{1B}(j)$ increases linearly with $j+\frac{1}{2}$ for low j values, with $c_{1A}=+1.70$, $c_{1B}=-1.70$ for $n=0$ according to calculations of Birge,[8] and $c_{1A}=+1.42$, $c_{1B}=-1.42$ for $n=1$, according to Hulthén.[9] For large j values, $F_{1A}-F_{1B}$ is no longer linear in j, but increases more and more slowly with j (cf. Table 7 of Hulthén's 1925 paper[10]).	$F_{2A}(j)-F_{2B}(j)\sim 0$ except in perturbations.[9]
CdH	Similar to HgH; $c_{1A}\backsim+0.3$, $c_{1B}\backsim-0.3$	$F_{2A}(j)-F_{2B}(j)\sim 0$
ZnH	Similar to HgH; $c_{1A}\backsim+0.15$, $c_{1B}\backsim-0.15$	$F_{2A}(j)-F_{2B}(j)\sim 0$
NO (lower ^2P)	$F_{1A}(j)-F_{1B}(j)\backsim+0.01j$	$F_{2A}(j)-F_{2B}(j)\backsim 0$
NO (upper ^2P)	$\lvert F_{1A}(j)-F_{1B}(j)\rvert\backsim 0.025j$ or $0.005j$	$F_{2A}(j)-F_{2B}(j)\backsim 0$
CaH	Doublet spacings apparently irregular	Irregular?
MgH	$F_{1A}(j)-F_{1B}(j)\backsim 0$ or slightly positive for small j until $j\backsim 10$, then becoming increasingly negative, approaching a value of about -0.4 for $j\geqq 18$.	$F_{2A}(j)-F_{2B}(j)$ small, negative, slightly more so than $F_{1A}(j)-F_{1B}(j)$
CH	$B^*_{1A}=14.207$; $B^*_{1B}=14.170$ (cf. VI, p. 799), hence $F_{1A}(j)>F_{1B}(j)$.	$B^*_{2A}=14.207$; $B^*_{2B}=14.170$(cf. VI, p. 799)

[4a] H. G. Gale and G. S. Monk, Astrophys. I. (in press).

[5] T. Hori, Zeits. f. Physik **44,** 845–6 (1927).

[6] Cf. II: Phys. Rev. **28,** 1202 (1926).

[7] E. Bengtsson and E. Hulthén, Zeits. f. Physik **52,** 275 (1928).

[8] According to Birge (Nat. Res. Council Report on Molecular Spectra, pp. 179–181, Eqs. (162), (163), and α' value on p. 181), the term values for the $n=0$ $^2P_{1/2}$ state of HgH (initial state of λ4017 band) can be represented by $F^{\pm}=B(j\pm\alpha)^2$, with $\alpha=0.130\pm0.005$. (Birge's F^+ with $B(j+\alpha)^2$, corresponds to F_A here, and his F^-, with $B(j-\alpha)^2$, to F_B here.) Putting $j+1/2$ in place of Birge's j, since the latter corresponds to the numbering of the old quantum theory, inserting $\alpha=0.130$, and $B=6.55$ from Birge's Eq. (162), and multiplying out, one gets

$$F_A(j)=C+B[j(j+1)]+1.70(j+1/2)$$
$$F_B(j)=C+B[j(j+1)]-1.70(j+1/2)$$

[9] E. Hulthén, Zeits. f. Physik **50,** 319 (1928).

[10] E. Hulthén, Zeits. f. Physik **32,** 32 (1925).

TABLE I. (continued.)

OH	$F_{1A}(j)-F_{1B}(j)\backsim+0.04j^2$ (cf. Table VII and Fig. 3 of VII)	$F_{2A}(j)-F_{2B}(j)$ negative to $j=4$, then positive, $\backsim 0.03j^2$ (cf. Table VII and Fig. 3 of VII; but cf. ref. 11 for correction)
BO	$F_{1A}(j)=F_{1B}(j)$	$F_{2A}(j)-F_{2B}(j)\backsim-0.026j$

c. ^3P states.

He_2 (cf. *e*, below); H_2 (cf. ref. 15*a*)

C_2 (Swan) and N_2 (second positive) bands[12]; in these $^3P\rightarrow{}^3P$ transitions, the observed σ-type doublets represent *differences* (or possibly sums) of separations for the initial and final ^3P terms, and so do not give direct information in regard to the individual ^3P levels.

In the C_2 bands, $\Delta E/B$ is probably fairly small so that the bands correspond closely for large j values to Hund's case *b*;[12, 13] the observed doublet separations are about equal in all the branches for large values of j; they are given[14] by $\Delta\nu\backsim 3.934\times10^{-4}j_k^2$. For small values of j, $\Delta\nu$ approaches zero for the R^c and R^v branches (and presumably also for the P^c and P^v branches, but they are not resolved), but for the R^r branches (presumably also for the P^r branches), $\Delta\nu$ approaches a constant value ($\Delta\nu\backsim 0.40$)[14] as j approaches 0.

In the second positive nitrogen bands,[12, 15] where the $\Delta E/B$ values are larger, the doublet

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[11] R. S. Mulliken, Phys. Rev. **32,** 997 (1928).

[12] Cf. R. S. Mulliken, Phys. Rev. **29,** 645–646 (1927).

[13] That Hund's case *b* is approached for large j values in the Swan bands is indicated by the fact that the triplets draw together and finally become unresolvable, as j increases, in both P and R branches. In the N_2 bands, the triplet separations slowly diminish with increasing j, but the triplets remain resolved to the end.

[14] Cf. J. D. Shea, Phys. Rev. **30,** 824 (1927). Shea's j is really $j_k''+1$. Shea's "stagger" is half the width $\Delta\nu$ of the σ-type doubling.—A re-examination of the data indicates that we have here a transition between two *inverted* ^3P levels, with the R^r branch corresponding to $^3P_0\rightarrow{}^3P_0$.

[15] A re-examination of the data (cf. ref. 12) on the second positive nitrogen bands shows that they are emitted in a transition between two *normal* ^3P states of fairly large ΔE, and that the P_3, R_3; P_2, R_2; P_1, R_1, branches respectively correspond to $^3P_2\rightarrow{}^3P_2$, $^3P_1\rightarrow{}^3P_1$, and $^3P_0\rightarrow{}^3P_0$ transitions (as supposed, but not proved, in ref. 12). The evidence is as follows: For small j, the ΔF values correspond to $^3P_{ab}$ initial and final states, i.e. ^3P states near case *a*, but with a tendency toward case *b* (cf. VII for corresponding discussion of doublet states). Thus it is possible to determine B^* values and j values. It is found that $B_3^*>B_2^*>B_1^*$, for both upper and lower ^3P states, also that $j=j_k-1$ for the P_3 and R_3 branches, $j=j_k$ for P_2 and R_2, $j=j_k+1$ for P_1 and R_1 (assuming that j_k (i.e. j_k' and j_k'') is the same for all three members of the natural triplets which exist for large j values, and that j is then equal to j_k for the middle component). Both these relations correspond to the identification of $F_3\rightarrow F_3$ with P_3 and R_3, and so on. (The relation $B^*(F_3)>B^*(F_2)>B^*(F_1)$ agrees with the theoretical work of Hill and Van Vleck (Phys. Rev. **32,** 261, 1928)). The evidence just given does not alone suffice to determine whether the triplets are normal or inverted. But according to Van Vleck's recent work (cf. preceding paper), we can identify the P_1 and R_1 branches with $^3P_0\rightarrow{}^3P_0$, and so on, on the basis of σ-type doubling data (cf. Table I, *c*). Hence $^3P_0$ corresponds to F_1, and so on, which means *normal* triplets.

It should be remarked that the missing lines give no support to this interpretation. The writer's Table I of ref. 12 is incorrect in respect to the missing lines predicted by the theory: the *predicted* values of j'' for the first lines of the P_1 and P_3 branches should be interchanged, and similarly for the R_1 and R_3 branches. (The j values given in Table I for the *observed* first lines are, however, correct.) The disagreements may probably be attributed to the expected weakness of the early lines of the P_1 and R_1 branches (j values very small) and to difficulties in interpretation caused by the large total number of lines present.

[15a] Cf. O. W. Richardson and K. Das, Proc. Roy. Soc. **122***A*, 688 (1929).

TABLE I. (continued.)

separations are vanishingly small for the P_3 and R_3 branches, just detectable for P_2 and R_2, and somewhat larger and independent of $j(\Delta\nu\backsim 0.24)$ for P_1 and R_1.

d. Case b ^2D state.

CH λ4300: $F_{1A}(j)=F_{1B}(j)$; $F_{2A}(j)=F_{2B}(j)$

e. He_2 bands.

Most of the He_2 levels (P and D states) show very wide σ-type doubling. The doublet widths increase rapidly with increase in the principal quantum number, and show a very varied behavior in different states.[16] As Weizel has shown,[17] these pecularities can be explained by a gradual uncoupling of σ from the molecular axis.

The He_2 bands fall into two groups, the "orthohelium" group of bands ("main series" and related bands) and the "parhelium" group ("second series" and related bands). The writer has hitherto assumed (ref. 16 and elsewhere[18]) that both groups represent singlet states of He_2, but others have fallen into the habit of assuming that the orthohelium levels are triplet states (with triplets so narrow as to be unresolved) and that the parhelium levels are singlet states. In view of Weizel's recent work,[17] it seems probable that these assumptions are correct.

For the relatively stable $2\,^3P$ state of He_2, according to Curtis, the σ-type doubling can be represented by a quadratic formula, with $F_A(j)>F_B(j)$: $B_A=7.334$, $B_B=7.310$, $c_A=c_B=0$. For other P and D states, the relations are more complicated,[16, 17] probably corresponding to various degrees of uncoupling of σ.

Eqs. (1)–(2), these two cases corresponding respectively to a σ-type doubling varying as $j(j+1)$ or as j. In some cases (especially He_2) both B^*'s and c's must be assumed to differ for the A and B substates.

Theory and conclusions: Hulthén has pointed out[19] that the selection rules of σ-type doubling can be expressed by a division of all the rotational states of a molecule into two practically non-combining systems of terms; combinations between such term-systems occur only in weak satellite branches[20] such as Q_{1A1B} and Q_{2A2B} of OH (cf. VII). Kronig[21] has made great progress in the theory of σ-type doubling, and has accounted for the observed selection rules for both homopolar and heteropolar molecules; he has also shown that the width of the σ-type doublets should vary as $j(j+1)$ in ^1P states. This is in agreement with the experimental data on AlH.[7] Van Vleck, in recent theoretical work (cf. preceding paper), has reached valuable conclusions in regard to the magnitude of the separations F_A-F_B to be expected in σ-type doubling, in the general case of molecules possessing a spin (cf. summary in section 8 of his paper).

One of the most striking relations in Table I is the contrast in certain case a ^2P states between the large separations F_A-F_B for the $^2P_{1/2}$ levels and the negligible separations for the $^2P_{3/2}$ levels. Examples are HgH, with

[16] Cf. R. S. Mulliken, Phys. Rev. **28**, 1215 (1926); W. E. Curtis, Proc. Roy. Soc. **118A**, 164–167 (1928); W. Weizel, ref. 17.

[17] W. Weizel, Zeits. f. Physik **52**, 175 (1928).

[18] Especially, Proc. Nat. Acad. Sci. **12**, 158 (1926).

[19] E. Hulthén, Zeits. f. Physik **46**, 349 (1928).

[20] Hulthén (ref. 19, bottom p. 351) mentions the occurrence of weak satellites of similar type in CH and MgH; apparently no published data exist in regard to these. According to Kronig (ref. 21, p. 353) such satellites must be attributed to the effect of external influences, such as electric fields, on the molecules.

[21] R. de L. Kronig, Zeits. f. Physik **46**, 814 (1928); **50**, 347 (1928).

a normal ^2P state, where the large separation is for $F_{1A}-F_{1B}(^2P_{1/2}$ levels); and BO, with an inverted ^2P, where the large separation is for $F_{2A}-F_{2B}$ (also $^2P_{1/2}$ levels). Evidently the case *a* designations $^2P_{1/2}$ and $^2P_{3/2}$ are more fundamental here than the essentially case *b* designations F_1 and F_2. In contrast to these results for case *a* ^2P states is the fact that near case *b* (OH, MgH, CH) the separations $F_{1A}-F_{1B}$ and $F_{2A}-F_{2B}$ are small and nearly equal. Analogous relations exist in the ^3P states of C_2 (case *b*) and N_2 (case *a*). All these conclusions are in excellent agreement with Van Vleck's theoretical work. Other relations shown in Table I, such as the linear variation of the doublet separations with j in case *a* $^2P_{1/2}$ states, and the tendency toward variation with $j(j+1)$ in ^1P states, are also in good agreement with Van Vleck's results. In the case of the second positive N_2 bands, Van Vleck's work makes it possible, as it was not previously, to conclude definitely that the ^3P levels involved are both normal.[15]

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January 29, 1929.

THE TWO QUANTUM EXCITED STATES OF THE HYDROGEN MOLECULE

By E. C. Kemble and C. Zener

Abstract

Theory of two quantum states of H_2.—There are sixteen possible wave functions for a pair of interacting H atoms which dissociate adiabatically into a normal H atom and a two quantum H atom. These wave functions give rise to eight distinct S states and four distinct P states (the latter are degenerate in the fixed nuclei problem). These states may be divided into four groups of three according to the symmetry of the wave functions with respect to (*a*) an interchange of electron coordinates, and (*b*) reflection in the plane which forms the perpendicular bisector of the internuclear axis. The *principles of selection* for transitions between these various types of electronic state are formulated and compared with the rules of Kronig. A first order *perturbation theory computation of the potential energy curves for the P states* shows that two of them have the form requisite for the formation of stable molecules. These two may be identified respectively with the C state (upper level for Werner bands) and the 2^3P state reported by Richardson. The agreement between the computed curves and the empirical data is fair.

Valence theory.—The computations show that in the case of the excited states of hydrogen the union of valence electrons to form symmetrical pairs is not the essential feature of molecule formation as London's original valence theory supposed. The rule that molecular formation is contingent on the removal of degeneracy from the wave functions of the interacting atoms seems to have a greater range of applicability than London's rule. The latter is no doubt correct for a great variety of cases, however.

Introduction

THE potential energy curves for the two sorts of interaction of normal hydrogen atoms have been calculated in first approximation according to the wave mechanics by Heitler and London,[1] Sugiura,[2] and Wang.[3] Heitler and London, whose work was completed by Sugiura, made a conventional application of the Schrödinger perturbation method to the problem, using as unperturbed wave functions those characteristic of the normal hydrogen atom. In the case of large internuclear distances such a first order calculation as theirs is sure to give somewhat too large an energy since the polarization van der Waals forces predominant at large distances are associated with the second and higher order terms in the perturbation theory.[4] Also in the limiting case where the nuclei are united to form a helium atom the computed energy is much too great at least for that solution of the problem which leads to molecular formation.[5] This might have been expected since the assumed

[1] W. Heitler and F. London, Zeits. f. Physik **44**, 455 (1927).

[2] Y. Sugiura, Zeits. f. Physik **45**, 484 (1927).

[3] S. C. Wang, Phys. Rev. **31**, 579 (1928).

[4] S. C. Wang, Phys. Zeits **28**, 663 (1927).

[5] Sugiura computed the energy in this limiting case and got very good agreement with the observed energy of normal helium. This agreement was due to an error, however, which was called to the attention of the authors by Prof. R. S. Mulliken. The computed energy when corrected is 10 volts too high.

unperturbed wave function in this limiting case is that for two non-repulsive electrons each in the field of a *singly* charged nucleus. This wave function is much more extended in space than the actual wave function and should give an excessively large energy value. In the region of nuclear separations near the normal separation for the molecule, however, the method gives a reasonable first approximation to the potential energy curve for the molecule as determined from the band spectrum.

Dr. Wang's calculation was carried out by the Ritz method and involves a well-chosen, but arbitrary assumption regarding the form of the wave function for the molecule. The polarization forces at large distances are partially included and the approximate wave function for the limiting case of the united atom is that used by Kellner,[6] so that it is not surprising to find that the method gives values of the molecular constants in better agreement with experiment than those predicted by Heitler, London, and Sugiura.

The present paper reports on an extension of the method of Heitler, London, and Sugiura to the case of certain excited states of the H_2 molecule which dissociate adiabatically into a normal H atom and a two quantum excited H atom. (At the time when the computation was begun we were not familiar with Wang's method and it seems now doubtful whether his method could be carried through with equal success if applied to our problem.) It is to be expected *a priori* that the approximation will be somewhat cruder for these excited states than for the normal molecule, because of the large polarizability of the two quantum H atom and the correspondingly large value of the van der Waals forces which must be neglected. The results are of interest, however, in their qualitative prediction regarding the nature of the different excited states of the molecule and in their bearing on the valence theory of London.[7]

Among the many different electronic levels of H_2 discovered by Richardson and other spectroscopic workers there are five which have been provisionally identified as "two quantum" levels.[8] Here we use the phrase "two quantum" to characterize molecular states which would dissociate into a normal atom and a two quantum atom if the nuclei were adiabatically separated. At least two of these levels combine freely with the normal state of the H_2 molecule as shown by the absorption measurements of Dieke and Hopfield.[9] We here adopt the notation of Dieke and Hopfield designating these two states by the symbols B and C, of which the former refers to the upper level of the Lyman bands and the latter to the upper level for the Werner bands. The normal state is called the A level and the system to which the Lyman bands belong is referred to as the B-A system.

The recent analysis of the fine structure of the Werner and Lyman bands (corrected as regards the latter series by Kemble and Guillemin[10]) makes it

[6] Kellner, Zeits. f. Physik **44**, 91 (1927).
[7] F. London, Zeits f. Physik **46**, 455 (1928); **50**, 24 (1928).
[8] R. T. Birge, Proc. Nat. Acad. Sci. **14**, 12 (1928).
[9] G. H. Dieke and J. J. Hopfield, Phys. Rev. **30**, 400 (1927).
[10] E. C. Kemble and Victor Guillemin, Jr., Proc. Nat. Acad. Sci. **14**, 782 (1928).

possible to draw approximate potential energy curves for the three electronic states A, B, C. (Cf. Fig. 1.) It also permits us to classify the A and B levels as ^1S type molecular states (without electronic angular momentum) and the C state as a ^1P state.[11] The computation described below was begun in the hope of accounting for the striking discrepancy between the potential energy curves for the B and C states. As the B state is very difficult to compute, the

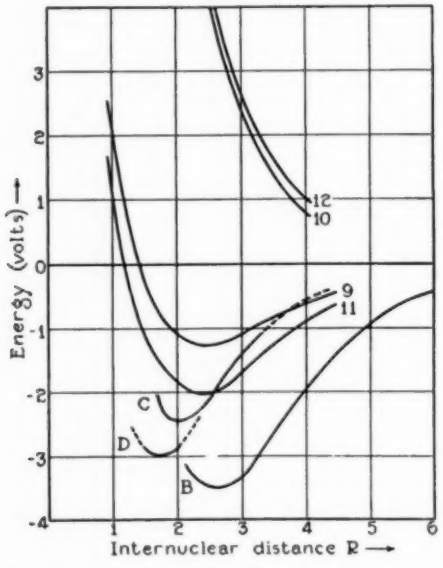

Fig. 1. Experimental and theoretical "potential" energy curves for two quantum states of H_4. Curves 9, 10, 11, 12 are drawn from the computed values of H_9^9, H_{10}^{10}, H_{11}^{11}, H_{12}^{12} respectively given in Table I. Curves B and C refer to the B and C states respectively and are based on empirical formulas of the type (38). Curve D is a fragment of the potential energy curve for the 2^3P state as computed from the empirical data of Richardson.

original project has been temporarily abandoned, however, and the authors have contented themselves with an approximate determination of the theoretical curves for the C state and three other states which, as it turns out, are closely related to it.

General Theory of Calcualtion

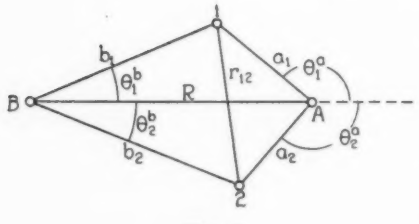

Fig. 2.

It is convenient to measure all distances in terms of the radius r_0 of the Bohr orbit for the normal state of the hydrogen atom and to measure energies in terms of the unit e^2/r_0 which is twice the ionization energy of the normal H atom. On this basis we let a_1, b_1, a_2, b_2 denote the distances of electrons number 1 and number 2 from the nuclei A

[11] The singlet character of the C state is deduced from the fact that it combines freely with the normal ^1S state whereas singlet triplet combinations should not occur in so light a molecule.

and B respectively. Let r_{12} be the distance between the electrons and R the distance between the nuclei. Then neglecting the electron spin the wave equation for the hydrogen molecule with fixed nuclei takes the form

$$\nabla_1^2\psi+\nabla_2^2\psi+2\left[E-\left(\frac{1}{R}+\frac{1}{r_{12}}-\frac{1}{a_1}-\frac{1}{a_2}-\frac{1}{b_1}-\frac{1}{b_2}\right)\right]\psi=0. \tag{1}$$

Following the procedure of Heitler and London we take as our initial set of approximate solutions of (1) the set obtained by multiplying the wave function for a free hydrogen atom successively by the different wave functions characteristic of a free hydrogen atom in one of the two-quantum states. Our "zero" approximations are then much better for large internuclear distances than for small. We denote the wave function for electron 1 on nucleus A in an unperturbed state with quantum numbers (n, l, m) by $\psi_1^a(n, l, m)$, that for electron 2 on nucleus B by $\psi_2^b(n, l, m)$, etc. Here m is the "magnetic" quantum number giving the orientation in space in the Bohr theory and associated with the azimuthal angle ϕ. It measures the angular momentum along the z axis which we identify with the internuclear axis. As the normal state of the H atom has zero orbital angular momentum, the m value for the two-quantum state becomes identical with the orbital electronic angular momentum of the molecule directed along the internuclear axis, i.e. with σ_k (Mulliken's notation). Taking all possible combinations of one electron in the normal one-quantum level and the other in one of the degenerate two-quantum states we obtain the following sixteen possible approximate solutions of (1).

$$\psi_1=\psi_1^a(1)\psi_2^b(2,0,0) \qquad \psi_5=\psi_2^a(1)\psi_1^b(2,0,0)$$
$$\psi_2=\psi_1^a(1)\psi_2^b(2,1,0) \qquad \psi_6=\psi_2^a(1)\psi_1^b(2,1,0)$$
$$\psi_3=\psi_1^a(1)\psi_2^b(2,1,1) \qquad \psi_7=\psi_2^a(1)\psi_1^b(2,1,1)$$
$$\psi_4=\psi_1^a(1)\psi_2^b(2,1,-1) \qquad \psi_8=\psi_2^a(1)\psi_1^b(2,1,-1)$$

$$\psi_9=\psi_1^b(1)\psi_2^a(2,0,0) \qquad \psi_{13}=\psi_2^b(1)\psi_1^a(2,0,0)$$
$$\psi_{10}=\psi_1^b(1)\psi_2^a(2,1,0) \qquad \psi_{14}=\psi_2^b(1)\psi_1^a(2,1,0)$$
$$\psi_{11}=\psi_1^b(1)\psi_2^a(2,1,1) \qquad \psi_{15}=\psi_2^b(1)\psi_1^a(2,1,1)$$
$$\psi_{12}=\psi_1^b(1)\psi_2^a(2,1,-1) \qquad \psi_{16}=\psi_2^b(1)\psi_1^a(2,1,-1)$$

Here

$$\psi_1^a(1)=\frac{1}{(\pi)^{1/2}}e^{-a_1},$$

$$\psi_1^a(2,0,0)=\frac{1}{(8\pi)^{1/2}}\left(1-\frac{a_1}{2}\right)e^{-a_1/2},$$

$$\psi_1^a(2,1,0)=\frac{1}{(32\pi)^{1/2}}a_1\cos\theta_1^a e^{-a_1/2},$$

$$\psi_1{}^a(2,1,1)=\frac{1}{(64\pi)^{1/2}}a_1 \sin\theta_1{}^a e^{i\phi_1-a_1/2},$$

$$\psi_1{}^a(2,1,-1)=\frac{1}{(64\pi)^{1/2}}a_1 \sin\theta_1{}^a e^{-i\phi_1-a_1/2},$$

etc. ϕ_1 and ϕ_2 denote the azimuthal angles of the electrons 1 and 2 respectively about the z axis which coincides with the interculear axis and has the direction $\overrightarrow{AB}$. The angles $\theta_1{}^a$, $\theta_2{}^a$, $\theta_1{}^b$, $\theta_2{}^b$ are defined by Fig. 1.

It is convenient to begin a perturbation calculation with approximate solutions of the differential equation which are mutually orthogonal. This condition of orthogonality is not satisfied by the functions $\psi_1, \psi_2, \cdots, \psi_{16}$, but we may readily form from them by linear combination sixteen other approximate solutions which have the same approximate energy value and which are mutually orthogonal. Thus we may take the four functions ψ_1, ψ_5, ψ_9, ψ_{13} and build up from them four others whose symmetry properties insure orthogonality. For example, the combinations

$$u_S=\psi_1+\psi_5=\psi_1{}^a(1)\psi_2{}^b(2,0,0)+\psi_2{}^a(1)\psi_1{}^b(2,0,0)$$
$$u_A=\psi_1-\psi_5=\psi_1{}^a(1)\psi_2{}^b(2,0,0)-\psi_2{}^a(1)\psi_1{}^b(2,0,0)$$

are respectively symmetric and antisymmetric with respect to an interchange of electronic coordinates, i.e., with respect to the transformation

$$\left.\begin{aligned} x_1', y_1', z_1' &= x_2, y_2, z_2 \\ x_2', y_2', z_2' &= x_1, y_1, z_1 \end{aligned}\right\} \qquad (E)$$

Similarly the combinations

$$\tilde{u}_S=\psi_1+\psi_9=\psi_1{}^a(1)\psi_2{}^b(2,0,0)+\psi_1{}^b(1)\psi_2{}^a(2,0,0)$$
$$\tilde{u}_A=\psi_1-\psi_9=\psi_1{}^a(1)\psi_2{}^b(2,0,0)-\psi_1{}^b(1)\psi_2{}^a(2,0,0)$$

are respectively symmetric and antisymmetric with respect to the transformation

$$\left.\begin{aligned} x_1', y_1', z_1' &= x_1, y_1, -z_1 \\ x_2', y_2', z_2' &= x_2, y_2, -z_2 \end{aligned}\right\} \qquad (N)$$

if the origin is taken at the midpoint of the internuclear axis and the z axis is chosen as stated above. The transformation (N) may be described either as a reflection in the median plane or as an interchange of nuclei with the understanding that the interchange of nuclei does not mean quite the same thing as it does in the free nuclei problem. We introduce the symbols S^E, A^E to indicate wave functions symmetric and antisymmetric with respect to transformation (E) respectively. S^N, A^N will be used to indicate the corresponding symmetries with respect to (n). Then clearly the following four

approximate solutions of (1) have the symmetries indicated and are mutually orthogonal.[12]

$$\begin{aligned} u_1&=g_1(\psi_1+\psi_5+\psi_9+\psi_{13}) && (S^E,S^N)\\ u_2&=g_2(\psi_1+\psi_5-\psi_9-\psi_{13}) && (S^E,A^N)\\ u_3&=g_3(\psi_1-\psi_5+\psi_9-\psi_{13}) && (A^E,S^N)\\ u_4&=g_4(\psi_1-\psi_5-\psi_9+\psi_{13}) && (A^E,A^N) \end{aligned}$$

Here g_1, g_2, g_3, g_4 are normalizing factors depending only on the parameter R. Similarly we may build up a set of four mutually orthogonal solutions from each of the other three types of two quantum hydrogen atom eigenfunctions. The three additional sets are

$$\begin{aligned} u_5&=g_5(\psi_2+\psi_6+\psi_{10}+\psi_{14}) && (S^E,A^N)\\ u_6&=g_6(\psi_2+\psi_6-\psi_{10}-\psi_{14}) && (S^E,S^N)\\ u_7&=g_7(\psi_2-\psi_6+\psi_{10}-\psi_{14}) && (A^E,A^N)\\ u_8&=g_8(\psi_2-\psi_6-\psi_{10}+\psi_{14}) && (A^E,S^N) \end{aligned}$$

$$\begin{aligned} U_9&=g_9(\psi_3+\psi_7+\psi_{11}+\psi_{15}) && (S^E,S^N)\\ U_{10}&=g_{10}(\psi_3+\psi_7-\psi_{11}-\psi_{15}) && (S^E,A^N)\\ U_{11}&=g_{11}(\psi_3-\psi_7+\psi_{11}-\psi_{15}) && (A^E,S^N)\\ U_{12}&=g_{12}(\psi_3-\psi_7-\psi_{11}+\psi_{15}) && (A^E,A^N) \end{aligned}$$

$$\begin{aligned} U_{13}&=g_{13}(\psi_4+\psi_8+\psi_{12}+\psi_{16}) && (S^E,S^N)\\ U_{14}&=g_{14}(\psi_4+\psi_8-\psi_{12}-\psi_{16}) && (S^E,A^N)\\ U_{15}&=g_{15}(\psi_4-\psi_8+\psi_{12}-\psi_{16}) && (A^E,S^N)\\ U_{16}&=g_{16}(\psi_4-\psi_8-\psi_{12}+\psi_{16}) && (A^E,A^N). \end{aligned}$$

The symmetry properties of these sixteen functions are shared by the exact solutions of the differential Eq. (1)[13] and hence these functions are particularly well fitted for use as first approximations. All functions of any one of the four symmetry types are orthogonal to all functions of each of the other types and all functions involving any given value of σ_k are orthogonal to all involving any other value of σ_k. Thus each of the functions U_9, $U_{10}, \cdots, U_{16}$ is orthogonal to all fifteen of the other functions, while the only pairs of functions not mutually orthogonal are (u_1, u_6), (u_2, u_5), (u_3, u_8), (u_4, u_7). From each of these pairs one may now form new linear combinations such as

[12] The product of any two functions, one of which is symmetric and the other antisymmetric with respect to a coordinate interchange such as (E) or (A), is antisymmetric with respect to the interchange and must therefore integrate to zero if the integral is extended over the region of definition.

[13] For example, if $\psi(x_i, y_i, z_i)$ is a solution of (1) substitution shows that

$$\psi^{(1)}(x_i, y_i, z_i)=\psi(x_i, y_i, -z_i)$$

is also a solution and has the same eigenwert. Hence either $\psi^{(1)}=\pm\psi$ or $\psi^{(1)}$ and ψ form a degenerate pair of solutions. In the former case ψ is either of the S^N or A^N type and in the latter case, which will occur only as a result of accidental degeneracy, we can form functions of the S^N and A^N type by taking linear combinations of $\psi^{(1)}$ and ψ.

$$U_1 = c_1^1 u_1 + c_6^1 u_6$$
$$U_6 = c_1^6 u_1 + c_6^6 u_6$$

which are mutual orthogonal and which have unimpaired symmetry. Thus one obtains the required set of sixteen completely orthogonal functions from which to build up the zero approximations to the solution of (1).

We now assume that the wave functions for the two quantum molecular states are of the form

$$\psi = \sum_{r=1}^{16} c_r U_r + v$$

where v is a small correction term orthogonal to $U_1, \cdots, U_{16}$ and approaching zero as the internuclear distance R is indefinitely increased. Writing the differential equation in the symbolic form

$$H\psi = E\psi \tag{4}$$

where

$$H = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) + \frac{1}{R} + \frac{1}{r_{12}} - \frac{1}{a_1} - \frac{1}{a_2} - \frac{1}{b_1} - \frac{1}{b_2} \tag{5}$$

and substituting from (3), we obtain

$$\sum_{r=1}^{16} c_r H U_r = \sum_{r=1}^{16} c_r E U_r + (E-H)v. \tag{6}$$

To determine the c's we multiply this equation by U_k^*, the complex conjugate of U_k, and integrate over the entire six dimensional space in which the wave functions are spread out. Let dV denote the element of volume and let H_r^k be the integral or matrix element $\int U_k^* H U_r dV$. The resulting equations then take the form

$$\sum_{r=1}^{16} c_r H_r^k = c_k E - \int U_k^* H v dV \qquad k = 1, 2, \cdots, 16. \tag{7}$$

As v is by hypothesis small, we may neglect the last term in getting a first approximation to a solution of the Eqs. (7) and thus obtain sixteen simultaneous homogeneous equations for the c's. These equations may also be obtained by a procedure which follows closely the standard perturbation method of the Schrödinger theory. The desired approximate energy values are the roots of the secular equation

$$\begin{vmatrix} H_1^1 - E & H_2^1 & H_3^1 & \cdot & \cdot \\ H_1^2 & H_2^2 - E & H_3^2 & \cdot & \cdot \\ H_1^3 & H_2^3 & H_3^3 - E & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix} = 0. \tag{8}$$

Fortunately most of the elements in this determinant vanish. For example, all matrix elements $H_r{}^k$ are zero for which U_k and U_r have different symmetries with respect to either of the transformations (E) or (N), since HU_r has the same symmetry as U_r itself. Thus our wave functions are divided into four equal groups with no matrix components corresponding to combinations between different groups.

Consider next one of these groups such as U_1, U_5, U_9, U_{13}, all members of which have the same symmetry. Matrix elements involving combinations of different members of the group are zero also when the functions U_k and U_r have different values of σ_k (i.e., different values of m for the primary two quantum wave function). It is sufficient to give the proof for the special element

$$H_9{}^{13} = \int U_{13}^* H U_9 dV$$

U_9 is a linear combination of the functions $\psi_3, \psi_7, \psi_{11}, \psi_{15}$. Remembering that $\psi_1{}^a(1), \psi_1{}^b(1), \psi_1{}^a(2), \cdots$, etc. are solutions of the wave equation for a single H atom we may use the relations

$$\begin{aligned} -\nabla_1{}^2\psi_1{}^a(1) &= 2E_1 + 2/a_1 \\ -\nabla_1{}^2\psi_1{}^b(1) &= 2E_1 + 2/b_1 \\ -\nabla_1{}^2\psi_1{}^a(2) &= 2E_2 + 2/a_1 \end{aligned} \tag{9}$$

and so on, where E_1 and E_2 are the energies of the normal state and of the first excited state of the hydrogen atom respectively. The sum of E_1 and E_2 is the "unperturbed" energy of the molecule and will be designated by E_0. Applying the operator H to U_9 we obtain

$$\begin{aligned} HU_9 = Hg_9[&\psi_1{}^a(1)\psi_2{}^b(2,1,1) + \psi_2{}^a(1)\psi_1{}^b(2,1,1) + \psi_1{}^b(1)\psi_2{}^a(2,1,1) \\ &+ \psi_2{}^b(1)\psi_1{}^a(2,1,1)] \end{aligned} \tag{10a}$$

$$\begin{aligned} = E_0 U_9 &+ \left(\frac{1}{R} + \frac{1}{r_{12}}\right) U_9 - g_9\left(\frac{1}{b_1} + \frac{1}{a_2}\right)[\psi_1{}^a(1)\psi_2{}^b(2,1,1) \\ &+ \psi_1{}^a(2,1,1)\psi_2{}^b(1)] - g_9\left(\frac{1}{b_2} + \frac{1}{a_1}\right)[\psi_2{}^a(1)\psi_1{}^b(2,1,1) \\ &+ \psi_2{}^a(2,1,1)\psi_1{}^b(1)]. \end{aligned} \tag{10b}$$

Clearly each term of HU_9 like each term in U_9 itself contains either $e^{i\phi_1}$ or $e^{i\phi_2}$ as a factor. Similarly each term in U_{13} contains $e^{-i\phi_1}$ or $e^{-i\phi_2}$. The angles ϕ_1 and ϕ_2 enter into the integrand $U_{13}^* H U_9$ only through these factors and through r_{12}. Changing the independent variables from ϕ_1 and ϕ_2 to

$$\begin{aligned} \phi &= \phi_1 \\ \chi &= \phi_2 - \phi_1 \end{aligned}$$

we observe that r_{12} depends only on χ while each term of $U_{13}^{*}HU_9$ contains one of the three factors

$$e^{-2i\phi_1}=e^{-2i\phi}$$
$$e^{-i(\phi_1+\phi_2)}=e^{-i\chi}\times e^{-2i\phi}$$
$$e^{-2i\phi_2}=e^{-2i\chi}\times e^{-2i\phi}$$

Hence in evaluating H_9^{13} we can factor out the integral $\int_0^{2\pi}e^{-2i\phi}d\phi$ which vanishes. The argument is easily extended to show that all matrix elements H_r^k vanish if U_k and U_r have different values of σ_k.

In consequence of the fact that most of the non-diagonal elements of the determinant (8) are zero, the determinant may be resolved into the product of the following factors:

$$\begin{gathered}(H_9^9-E)\ ;\ (H_{10}^{10}-E)\ ;\ (H_{11}^{11}-E)\ ;\ (H_{12}^{12}-E)\ ;\ (H_{13}^{13}-E)\ ;\\ (H_{14}^{14}-E)\ ;\ (H_{15}^{15}-E)\ ;\ (H_{16}^{16}-E)\ ;\ \begin{vmatrix} H_1^1-E & H_6^1 \\ H_1^6 & H_6^6-E \end{vmatrix}\ ;\\ \begin{vmatrix} H_2^2-E & H_5^2 \\ H_2^5 & H_5^5-E \end{vmatrix}\ ;\ \begin{vmatrix} H_3^3-E & H_8^3 \\ H_3^8 & H_8^8-E \end{vmatrix}\ ;\ \begin{vmatrix} H_4^4-E & K_7^4 \\ H_4^7 & H_7^7-E \end{vmatrix}\ .\end{gathered} \tag{11}$$

Each energy level is obtained by setting one factor equal to zero.

As the functions U_9, U_{10}, U_{11}, U_{12} differ from the corresponding functions U_{13}, U_{14}, U_{15}, U_{16} respectively only in the sign of the exponent in the factor $e^{\pm i\phi}$, it is clear that

$$H_9^9=H_{13}^{13}\ ;\quad H_{10}^{10}=H_{14}^{14}\ ;\quad H_{11}^{11}=H_{15}^{15}\ ;\quad H_{12}^{12}=H_{16}^{16}$$

Hence the first eight factors of the set (11) vanish in pairs. The corresponding energy levels are consequently degenerate and the eigenfunctions are indeterminate. Suppose, for example, that

$$H_9^9-E=H_{13}^{13}-E=0.$$

Then in (7) all the coefficients c_r must vanish except c_9 and c_{13} which are undetermined except for the normalization condition on

$$\psi=c_9U_9+c_{13}U_{13}.$$

These degenerate states are those of the P type with $\sigma_k=\pm 1$. The degeneracy is removed when the rotation of the nuclei is taken into account and its removal gives rise to the "sigma-type doubling."[14]

By setting any one of the last four factors in the group (11) equal to zero we locate two energy levels of the S type (with $\sigma_k=0$). Thus there are in all twelve distinguishable energy levels of which four are degenerate and of the P type while the other eight are of the S type. There are two S states and one P state for each of the four types of symmetry. (Of course many of

[14] E. L. Hill and J. H. Van Vleck, Phys. Rev. **32**, 250 (1928); R. de L. Kronig, Zeits f. Physik **50**, 347 (1928).

these "states" represent possible collision types for interacting hydrogen atoms which involve an almost purely repulsive force and hence could not yield stable molecules.)

It is well known that in light atoms where the interaction of spin and orbital motion is very slight transitions between singlet and triplet states occur with great infrequency. As the two electron symmetries S^E and A^E correspond to singlet and triplet states respectively (Pauli principle) and as we are dealing with the lightest of molecules, it is clear that jumps between states of different electron symmetry should be negligible.

The principles of selection for symmetrical diatomic molecules have been discussed by Hund [15] and Kronig[16] using as a basis for argument the complete eigenfunctions for the molecule with free rotating nuclei. Rules governing the transitions between electronic states can be derived even more simply and directly on the basis of the fixed nuclei problem. As the electronic eigenfunction are but little distorted by slow nuclear rotation we may infer that the principles of selection so derived will hold at least approximately when applied to actual molecules.

If we treat the nuclei as fixed, place the origin at a point midway between them and use the internuclear axis as the z axis for a set of spherical coordinates, the expressions for the components of the classical electric moment become

$$P_x = \sum_i e r_i \sin\theta_i \cos\phi_i,$$

$$P_y = \sum_i e r_i \sin\theta_i \sin\phi_i,$$

$$P_z = \sum_i e r_i \cos\theta_i.$$

The formation of matrices from the three functions P_x, P_y, P_z leads to the following selection rules. (a) When $\Delta\sigma_k$ is zero the matrix elements of P_x and P_y always vanish, while those of P_z are also zero unless the two electronic wave functions concerned have opposite symmetry with respect to the median plane. (b) When $\Delta\sigma_k$ is ± 1 the matrix elements of P_z always vanish, while those of P_x and P_y are zero unless the electronic wave functions have the *same* symmetry with respect to the median plane. Thus the permitted transitions reduce to the following:

$$A^N \longleftrightarrow S^N \qquad \text{if} \qquad \Delta\sigma_k = 0\ ; \tag{12}$$

$$\left.\begin{matrix} S^N \longleftrightarrow S \\ A^N \longleftrightarrow A^N \end{matrix}\right\} \qquad \text{if} \qquad \Delta\sigma_k = \pm 1. \tag{13}$$

[15] F. Hund, Zeits f. Physik **42**, 93 (1927); R. de L. Kronig, Zeits f. Physik **46**, 814 (1928).

[16] Kronig proves only approximate symmetry and approximate anti-symmetry with respect to β, but an examination of the differential equation shows that these symmetry properties are rigorous. This point was brought to the attention of the writers by Professor Kramers.

The method of deriving the above principles of selection may be made rigorous with the aid of the α and β transformations of Kronig. Successive rotational levels for any electronic state of a free molecule have alternating symmetry with respect to the α transformation and with respect to the β transformation. The transformation (N) above is equivalent to the resultant of the α and β transformations. Hence if any rotational state is α-symmetric and also β-symmetric, the associated unperturbed electronic eigenfunction U_r must have the symmetry S^N. Conversely if U_r has the symmetry S^N, each rotational sublevel will have the same symmetry with respect to the α and β transformations, while if U_r has the symmetry A^N, each rotational sublevel will have opposite symmetry with respect to α and β transformations. Consider next a transition for which $\Delta\sigma_k$ vanishes. Then if the jump is to be permitted the upper and lower rotational levels must have the same symmetry with respect to α and opposite symmetry with respect to β. In order to satisfy these conditions simultaneously, it is necessary that in one case the symmetry of the sublevel shall be the same with respect to α as with respect to β, while in the other case the symmetry with respect to α must be opposite to that with respect to β. This leads at once to the principle of selection (12). The rule (13) can be derived in the same way. As every eigenfunction is rigorously symmetrical or antisymmetrical with respect to α and to β,[16] it is clear that our rules are not affected by the distortion of U_r due to nuclear rotation. Kronig does not call specific attention to the fact that in the case of symmetric molecules the existence of both α and β types of symmetry leads to these principles of selection for electronic levels.

As the normal state of the hydrogen molecule has the symmetry (S^E, S^N) it follows that of the twelve possible two quantum molecular states there is just one of the P type which should combine with the normal state to produce a band system. This state must have the symmetry (S^E, S^N) also and its energy is therefore approximately $H_9{}^9$. This must be the "C" state which forms the upper energy level for the Werner bands.

On the other hand there are two possible molecular levels of the S type having the appropriate symmetry (S^E, A^N) for the production of jumps to and from the normal state. Their energies are the roots of the equation

$$\begin{vmatrix} H_2{}^2-E & H_5{}^2 \\ H_2{}^5 & H_5{}^5-E \end{vmatrix} = 0. \tag{14}$$

One of these must be the B state which forms the upper level of the $A-B$ system of Dieke and Hopfield to which the Lyman bands belong.

Computation of Approximate Energy of P Type States

It remains to evaluate the matrix elements H_k and thus to determine the theoretical potential energy curves for the various two quantum electronic states. This we have done for the P type states only. The labor involved in the calculation was considerable and would have been even greater for the S states.

With the aid of Eq. (10c) the following expression for H_9^9 may be derived:

$$H_9^9 = \int U_9^* H U_9 dV = E_0 + R^{-1} + \int U_9^* U_9 r_{12}^{-1} dV$$
$$- g_9^2 \int \left\{ \left[\frac{1}{a_1} + \frac{1}{b_2} \right] [\psi_2^a(1)\psi_1^b(2) + \psi_2^a(2)\psi_1^b(1)] \right.$$
$$\left. + \left[\frac{1}{a_2} + \frac{1}{b_1} \right] [\psi_1^a(1)\psi_2^b(2) + \psi_1^a(2)\psi_2^b(1)] \right\} \frac{U_9^*}{g_9} dV. \quad (15)$$

Denote the first of the two integrals in the right-hand member of (15) by K and the second by J. The latter may be split into convenient terms if we write U_9 in terms of the primary ψ functions and multiply out. Terms involving the product of two ψ's with the same subscript but different quantum numbers integrate to zero. For example,

$$\int \left(\frac{1}{a_1} + \frac{1}{b_2} \right) \psi_2^a(1)\psi_1^b(2)\overset{*}{\psi}_1^a(1)\overset{*}{\psi}_2^b(2) dV$$
$$= \frac{1}{8\pi^2} \int \left(\frac{1}{a_1} + \frac{1}{b_2} \right) \sin\theta_1^b \sin\theta_2^b b_1 b_2 e^{-[a_1 + a_2 + (b_1 + b_2)/2]} e^{i(\phi_1 - \phi_2)} dV. \quad (16)$$

Here

$$dV = a_1^2 \sin\theta_1 da_1 d\theta_1 d\phi_1 a_2^2 \sin\theta_2 da_2 d\theta_2 d\phi_2$$

Clearly we can factor out the integral

$$\int_0^{2\pi} \int_0^{2\pi} e^{i(\phi_1 - \phi_2)} d\phi_1 d\phi_2$$

which vanishes.

A number of the other terms are easily seen to be equivalent and the integral J can be reduced to the form

$$J = 4g_9^2(J_1 + J_2) \quad (17)$$

where

$$J_1 = \int \left(\frac{1}{a_1} + \frac{1}{b_2} \right) \psi_1^b(1)\overset{*}{\psi}_1^b(1)\psi_2^a(2)\overset{*}{\psi}_2^a(2) dV \quad (17a)$$

$$J_2 = \int \left(\frac{1}{a_2} + \frac{1}{b_1} \right) \psi_1^b(1)\overset{*}{\psi}_1^a(1)\psi_2^a(2)\overset{*}{\psi}_2^b(2) dV. \quad (17b)$$

Similarly K is reducible to the form

$$K = 4g_9^2(K_1 + K_2 + K_3 + K_4) \quad (18)$$

where

$$K_1 = \int \frac{\psi_1^b(1)\overset{*}{\psi}_1^b(1)\psi_2^a(2)\overset{*}{\psi}_2^a(2)}{r_{12}} dV; \quad (19a)$$

$$K_2=\int\frac{\psi_1{}^b(1)\overset{*}{\psi}_1{}^a(1)\psi_-{}^a(2)\overset{*}{\psi}_2{}^b(2)}{r_{12}}dV\ ; \tag{19b}$$

$$K_3=\int\frac{\psi_1{}^a(1)\overset{*}{\psi}_1{}^a(2)\psi_2{}^b(2)\overset{*}{\psi}_2{}^b(1)}{r_{12}}dV\ ; \tag{19c}$$

$$K_4=\int\frac{\psi_1{}^b(1)\overset{*}{\psi}_1{}^a(2)\psi_2{}^a(2)\overset{*}{\psi}_2{}^b(1)}{r_{12}}dV\ ; \tag{19d}$$

Putting these results together and remembering that E_0 is the sum of the energies of a normal H atom and an H atom in a two-quantum state expressed in terms of the unit e^2/a_0, we have

$$H_9{}^9=-5/8+R^{-1}-4g_9{}^2[J_1+J_2-(K_1+K_2+K_3+K_4)] \tag{20}$$

In the same way we deduce

$$H_{10}{}^{10}=-5/8+R^{-1}-4g_{10}{}^2[J_1-J_2-(K_1-K_2-K_3+K_4)]\ ; \tag{21}$$

$$H_{11}{}^{11}=-5/8+R^{-1}-4g_{11}{}^2[J_1+J_2-(K_1+K_2-K_3-K_4)]\ ; \tag{22}$$

$$H_{12}{}^{12}=-5/8+R^{-1}-4g_{12}{}^2[J_1-J_2-(K_1-K_2+K_3-K_4)]. \tag{23}$$

Thus the integrals to be evaluated for $H_{10}{}^{10}$, $H_{11}{}^{11}$, and $H_{12}{}^{12}$ are the same as those needed for $H_9{}^9$.

The required integrals may be computed most easily by the use of elliptic coordinates. Let us begin with the determination of the normalizing factor g_9. It is fixed by the condition

$$\int U_9^*U_9dV=g_9{}^2\int(\psi_3\overset{*}{\psi}_3+\psi_7\overset{*}{\psi}_7+\psi_{11}\overset{*}{\psi}_{11}+\psi_{15}\overset{*}{\psi}_{15}+\psi_3\overset{*}{\psi}_7+\psi_7\overset{*}{\psi}_3+\psi_3\overset{*}{\psi}_{11}+\psi_{11}\overset{*}{\psi}_3$$
$$+\psi_3\overset{*}{\psi}_{15}+\psi_{15}\overset{*}{\psi}_3+\psi_7\overset{*}{\psi}_{11}+\psi_{11}\overset{*}{\psi}_7+\psi_{15}\overset{*}{\psi}_7+\psi_7\overset{*}{\psi}_{15}+\psi_{11}\overset{*}{\psi}_{15}+\psi_{15}\overset{*}{\psi}_{11})dV.$$

As ψ_3, ψ_7, ψ_{11}, ψ_{15} are separately normalized we may reduce the above to the form

$$2g_9{}^2\left[2+\int(\psi_3\overset{*}{\psi}_{11}+\psi_7\overset{*}{\psi}_{15})dV\right]=1$$

or

$$g_9{}^2=\frac{1}{4(1+F)} \tag{24}$$

where

$$F=\int\psi_3\overset{*}{\psi}_{11}dV=\int\psi_7\overset{*}{\psi}_{15}dV=\int\psi_1{}^a(1)\overset{*}{\psi}_1{}^b(1)dV_1\int\psi_2{}^a(2)\overset{*}{\psi}_2{}^b(2)dV_2$$

Introducing the elliptic coordinates

$$\lambda=\frac{a+b}{R}\ ;\quad \mu=\frac{a-b}{R}\ ;\quad dV=\frac{R^3(\lambda^2-\mu^2)}{8}d\lambda d\mu d\phi,$$

we obtain

$$\int \psi_1^a(1)\overset{*}{\psi}_1^b(1)dV_1=\frac{R^3}{8\pi}\int_{+1}^{\infty}d\lambda_1\int_{-1}^{+1}d\mu_1\int_0^{2\pi}d\phi_1(\lambda_1^2-\mu_1^2)e^{-\lambda_1 R}$$
$$=e^{-R}(1+R+R^2/3).$$

Similarly

$$\int \psi_2^a(2)\overset{*}{\psi}_2^b(2)dV_2=\frac{R^5}{16\times 64}\int_1^{\infty}e^{-R\lambda_2/2}(\lambda_2^2-1)d\lambda_2\int_{-1}^{+1}(\lambda_2^2-\mu_2^2)(1-\mu_2^2)d\mu_2$$
$$=e^{-R/2}\left(1+\frac{R}{2}+\frac{R^2}{10}+\frac{R^3}{120}\right).$$

Finally

$$F=e^{-3R/2}(1+R+R^2/3)(1+R/2+R^2/10+R^3/120). \tag{25}$$

The same procedure applied to the other normalizing factor yields

$$g_{11}^2=g_9^2\ ;\qquad g_{12}^2=g_{10}^2=\frac{1}{4(1-F)}\ . \tag{26}$$

Inspection of (17a) shows that

$$J_1=\int\frac{\psi_1^b(1)\overset{*}{\psi}_1^b(1)}{a_1}dV_1+\int\frac{\psi_2^a(2)\overset{*}{\psi}_2^a(2)}{b_2}dV_2.$$

Both of these integrals are easily evaluated. We find

$$\int\frac{\psi_1^b(1)\overset{*}{\psi}_1^b(1)}{a_1}dV_1=\frac{R^2}{2}\int_1^{\infty}d\lambda\int_{-1}^{+1}(\lambda-\mu)e^{-R(\lambda-\mu)}d\mu=\frac{1}{R}-e^{-2R}\left(1+\frac{1}{R}\right).$$

$$\int\frac{\psi_2^a(2)\overset{*}{\psi}_2^a(2)}{b_2}dV_2=\frac{R^4}{8\times 64}\int_1^{\infty}d\lambda e^{-R\lambda/2}(\lambda^2-1)\int_{-1}^{+1}e^{-R\mu/2}(\lambda+\mu)(1-\mu^2)d\mu$$
$$=\frac{1}{R}-\frac{6}{R^3}+\frac{e^{-R}}{4}\left(1+\frac{8}{R}+\frac{24}{R^2}+\frac{24}{R^3}\right).$$

Thus

$$J_1=\frac{2}{R}-\frac{6}{R^3}+\frac{e^{-R}}{4}\left(1+\frac{8}{R}+\frac{24}{R^2}+\frac{24}{R^3}\right)-e^{-2R}\left(1+\frac{1}{R}\right). \tag{27}$$

The evaluation of J_2 proceeds along lines similar to that of J_1 and presents no features of interest. The result is

$$J_2=e^{-3R/2}\left[(1+R)\left(1+\frac{R}{2}+\frac{R^2}{10}+\frac{R^3}{120}\right)+\left(1+R+\frac{R^2}{3}\right)\left(1+\frac{R}{2}+\frac{R^2}{12}\right)\right]. \tag{28}$$

K_1 gives the mutual potential energy of two static charge distributions of density $\psi_1^b(1)\overset{*}{\psi}_1^b(1)$ and $\psi_2^a(2)\overset{*}{\psi}{}^a(2)$ respectively. The first distribution is

spherical and its potential at a point distant b_2 from the nucleus b is easily seen to be

$$4\int_0^{b_2}\frac{b^2e^{-2b}}{b_2}db+4\int_{b_2}^{\infty}be^{-2b}db=\frac{1}{b_2}-e^{-2b_2}\left(1+\frac{1}{b_2}\right).$$

Multiplying this potential by the density of the second charge distribution and integrating we obtain

$$K_1=\frac{1}{64\pi}\int\frac{a_2^2\sin^2\theta_2{}^a e^{-a_2}}{b_2}\left[1-e^{-2b_2}(1+b_2)\right]dV_2.$$

Transforming to elliptic coordinates and using the relation

$$\sin^2\theta^a=\frac{(\lambda^2-1)(1-\mu^2)}{(\lambda+\mu)^2}$$

one obtains

$$\begin{aligned}K_1=&\frac{1}{R}-\frac{6}{R^3}-\frac{4}{27}e^{-R}\left(1+\frac{16}{R}+\frac{112}{3R^2}+\frac{112}{3R^3}\right)\\&+\frac{1}{27}e^{-2R}\left(1+\frac{9}{R}+\frac{76}{3R^2}+\frac{38}{3R^3}\right).\end{aligned}\tag{29}$$

K_3 may be dealt with in a manner similar to that used in connection with K_1.

$$K_3=\frac{1}{64\pi^2}\int\frac{e^{-3/2a_1}a_1\sin\theta_1{}^a e^{-i\phi_1}e^{-3/2b_2}b_2\sin\theta_2{}^b e^{i\phi_2}}{r_{12}}dV_1dV_2.$$

The integral is resolved into real and imaginary parts by means of the relation

$$e^{i(\phi_2-\phi_1)}=\cos(\phi_2-\phi_1)+i\sin(\phi_2-\phi_1)$$

As the angles ϕ_1 and ϕ_2 enter the integrand only through r_{12}, which is independent of the sign of $\phi_2-\phi_1$, and through the exponential $e^{i(\phi_2-\phi_1)}$, it is evident that the imaginary part of the integral must vanish. Expanding $\cos(\phi_2-\phi_1)$ into the sum of $\cos\phi_1\cos\phi_2$ and $\sin\phi_1\sin\phi_2$ we break K_3 into the sum of the two integrals

$$K_3'=\frac{1}{64\pi^2}\int\left[\frac{e^{-3b_1/2}b_2\sin\theta_2{}^b\cos\phi_2}{r_{12}}\right]\left[e^{-3a_1/2}a_1\sin\theta_1{}^a\cos\phi_1\right]dV_1dV_2$$

$$K_3''=\frac{1}{64\pi^2}\int\left[\frac{e^{-3b_2/2}b_2\sin\theta_2{}^b\sin\phi_2}{r_{12}}\right]\left[e^{-3a_1/2}a_1\sin\theta_1{}^a\sin\phi_1\right]dV_1dV_2.$$

Let P be the potential at the point b_1, $\theta_1{}^b$, ϕ_1 due to the distribution of charge $e^{-2b_2/2}b_2\sin\theta_2{}^b\cos\phi_2$. Then

$$K_3'=\frac{1}{64\pi^2}\int Pe^{-3a_1/2}a_1\sin\theta_1{}^a\cos\phi_1dV_1$$

As $\sin\theta_2{}^b\cos\phi_2$ is a spherical harmonic of the first order, we have[17]

$$P=\frac{4\pi}{3}\sin\theta_1{}^b\cos\phi_1\left\{b_1\int_{b_1}^{\infty}e^{-3b_2/2}b_2db_2+\frac{1}{b_1{}^2}\int_0^{b_1}e^{-3b_2/2}b_2{}^4db_2\right\}.$$

K_3' becomes

$$K_3'=\frac{1}{36\pi}\int e^{-3a_1/2}a_1\sin\theta_1{}^a\sin\theta_1{}^b\cos^2\phi_1\left\{\frac{64}{27}b_1{}^2-e^{-3b_1/2}\left(b_1+\frac{8}{3}\right.\right.$$
$$\left.\left.+\frac{32}{9b_1}+\frac{64}{27b_1{}^2}\right)\right\}dV_1$$

K_3'' is identical with K_3' except for the substitution of $\sin^2\phi_1$ for $\cos^2\phi_1$ in the integrand. Adding the integrands eliminates ϕ_1 entirely. Introducing elliptic coordinates, integrating with respect to ϕ_1, and making the additional transformation

$$x=\mu\ ;\qquad y=\lambda-\mu$$

we obtain

$$K_3=\frac{R^3}{64}\int_{-1}^{+1}e^{-3Rx/2}(1-x^2)\int_{1-x}^{\infty}F(y)dy,$$

where

$$F(y)=\frac{64}{27R}e^{-3Ry/4}\left(\frac{\alpha}{y^2}+\frac{\beta}{y}+\gamma+y\right)-e^{-3Ry/2}\left\{\frac{R^2}{8}(\alpha y+\beta y^2+\gamma y^3+y^4)\right.$$
$$+\frac{2R}{3}(\alpha+\beta y+\gamma y^2+y^3)+\frac{16}{9}\left(\frac{\alpha}{y}+\beta+\gamma y+y^2\right)$$
$$\left.+\frac{64}{27R}\left(\frac{\alpha}{y^2}+\frac{\beta}{y}+\gamma+y\right)\right\}\ ;$$

and

$$\alpha=2x(x^2-1)\ ;\quad \beta=5x^2-1\ ;\quad \gamma=4x$$

Let $\phi(x)$ be the function

$$\phi(x)=\int_{1-x}^{\infty}F(y)dy.$$

A tedious integration yields

$$\phi(x)=\frac{16}{9}\left(\frac{4\beta}{3}-\alpha\right)\left\{E_i\left[-\frac{3R(1-x)}{2}\right]-E_i\left[-\frac{3R(1-x)}{4}\right]\right\}$$
$$+\frac{64}{27R}e^{-3R(1-x)/4}\left(\alpha+\frac{4}{3R}\gamma+\frac{16}{9R^2}+\frac{4(1-x)}{3R}\right)$$

[17] Cf. J. H. Jeans, Electricity and Magnetism, p. 224 Camb. Univ. Press, 1923.

$$-\frac{2}{3R}e^{-3R/2(1-x)}\left[\left(u_0+\frac{2}{3R}u_1+\frac{32\alpha}{9}+\frac{8}{9}\,\frac{u_2}{R^2}+\frac{16u_3}{9R^3}+\frac{128}{27R^4}\right)\right.$$
$$+\left(u_1+\frac{4u_2}{3R}+\frac{8u_3}{9R^2}+\frac{8}{9R^3}\right)(1-x)+\left(u_2+\frac{2u_3}{R}+\frac{2}{3R^2}\right)(1-x)^2 \qquad (30)$$
$$\left.+\left(u_3+\frac{1}{R}\right)(1-x)^3+\frac{3R}{16}(1-x)^4\right].$$

Here $Ei(x)$ is the integral logarithm of x and

$$u_0=\frac{2\alpha}{3}+\frac{16\beta}{9}+\frac{64\gamma}{27};$$
$$u_1=\frac{\alpha}{8}+\frac{2\beta}{3}+\frac{16\gamma}{9}+\frac{64}{27};$$
$$u_2=\frac{\beta}{8}+\frac{2\gamma}{3}+\frac{16}{9};$$
$$u_3=\frac{\gamma}{8}+\frac{2}{3}$$

K_3 is now given by

$$K_3=\frac{R^3}{72}\int_{-1}^{+1}e^{-3Rx/2}(1-x^2)\phi(x)dx. \qquad (31)$$

The last quadrature indicated in the above equation has been carried through graphically.

In order to evaluate K_2 and K_4 we have found it necessary to follow Sugiura[2] in using Neumann's expansion of $1/r_{12}$ in harmonics of $\phi_2-\phi_1$. This is

$$1/r_{12}=\frac{2}{R}\sum_{\tau=0}^{\infty}\sum_{\nu=0}^{\infty}D_{\tau\nu}P_\tau^\nu\binom{\lambda_1}{\lambda_2}Q_\tau^\nu\binom{\lambda_2}{\lambda_1}P_\tau^\nu(\mu_1)P_\tau^\nu(\mu_2)\cos\nu(\phi_2-\phi_1) \qquad (32)$$

where P_τ^ν and Q_τ^ν are associated Legendre functions of the first and second kind respectively and $D_{\tau\nu}$ is given by

$$D_{\tau\nu}=(-1)^\nu\epsilon_\nu\frac{2\tau+1}{2}\left(\frac{\Pi(\tau-\nu)}{\Pi(\tau+\nu)}\right)^2, \quad \epsilon_0=1; \quad \epsilon_1=\epsilon_2=\cdots=2.$$

The upper arguments of $P_\tau^\nu\binom{\lambda_1}{\lambda_2}$ and $Q_\tau^\nu\binom{\lambda_2}{\lambda_1}$ in (32) apply when $\lambda_2>\lambda_1$ and the lower arguments when $\lambda_2<\lambda_1$. Using elliptic coordinates K_2 takes the form

$$K_2=\frac{R^8}{(128)^2\pi^2}\int\frac{e^{-(\lambda_1R+\lambda_2R/2)}}{r_{12}}(\lambda_2^2-1)(1-\mu_2^2)(\lambda_1^2-\mu_1^2)(\lambda_2^2-\mu_2^2)d\lambda_1\cdots d\phi_2 \qquad (33)$$

and as the angles ϕ_1 and ϕ_2 enter the integrand only through the expansion (32) it is clear that integration over these angles will reduce all terms to zero except that for which ν is zero. The corresponding term of (32) is simply

$$\frac{2}{R}\sum_{\tau=0}^{\infty}\left(\frac{2\tau+1}{2}\right)P_\tau\binom{\lambda_1}{\lambda_2}Q_\tau\binom{\lambda_2}{\lambda_1}P_\tau(\mu_1)P_\tau(\mu_2).$$

Inserting this term for $1/r_{12}$ in (33) and integrating with respect to μ_1, we observe that

$$\int_{-1}^{+1}P_\tau(\mu_1)(\lambda_1^2-\mu_1^2)d\mu_1=2(\lambda_1^2-1/3)\quad\text{if}\quad\tau=0,$$
$$=-4/15\qquad\text{if}\quad\tau=2,$$

and vanishes for all other values of τ. Hence K_2 breaks into two integrals, one for $\tau=0$, the other for $\tau=2$. Designating these as $K_2^{(0)}$ and $K_2^{(2)}$ respectively, we have

$$K_2^{(0)}=\frac{R^7}{32\times64}\int P_0\binom{\lambda_1}{\lambda_2}Q_0\binom{\lambda_2}{\lambda_1}P_0(\mu_2)e^{-(\lambda_1R+\lambda_2R/2)}$$
$$(\lambda_2^2-1)(1-\mu_2^2)(\lambda_2^2-\mu_2^2)(\lambda_1^2-\tfrac{1}{3})d\lambda_1d\lambda_2d\mu_2$$

$$K_2^{(2)}=\frac{-R^7}{48\times64}\int P_2\binom{\lambda_1}{\lambda_2}Q_2\binom{\lambda_2}{\lambda_1}P_2(\mu_2)e^{-(\lambda_1R+\lambda_2R/2)}$$
$$(\lambda_2^2-1)(1-\mu_2^2)(\lambda_2^2-\mu_2^2)d\lambda_1d\lambda_2d\mu_2.$$

Inserting the values of the Legendre functions,[18] viz.,

$$P_0(x)=1\ ;\qquad P_2(x)=(3x^2-1)/2\ ;$$
$$Q_0(x)=ln\left(\frac{x+1}{x-1}\right);\qquad Q_2(x)=-3x+\frac{3x^2-1}{2}ln\left(\frac{x+1}{x-1}\right),$$

and integrating with respect to μ_2 we obtain

$$K_2^{(0)}=\frac{R^7}{24\times64}\int_{+1}^{\infty}d\lambda_2(\lambda_2^2-1)(\lambda_2^2-\tfrac{1}{3})e^{-\lambda_2R/2}$$
$$\left\{\int_{\lambda_2}^{\infty}e^{-\lambda_1R}\ln\left(\frac{\lambda_1+1}{\lambda_1-1}\right)\left(\lambda_1^2-\frac{1}{3}\right)d\lambda_1\right.$$
$$\left.+\ln\left(\frac{\lambda_2+1}{\lambda_2-1}\right)\int_1^{\lambda_2}e^{-\lambda_1R}\left(\lambda_1^2-\frac{1}{3}\right)d\lambda_1\right\}.$$

Another tedious integration yields

$$K_2^{(0)}=\frac{1}{24}\left[e^{-R/2}\left\{Q\left(S\left[C+ln\frac{2R}{3}\right]-S'E_i(-2R)\right)\right.\right.$$
$$\left.\left.+S\left(e^RE_i(-R)Q'-\left[\frac{2R^2}{15}+\frac{31R}{15}+\frac{356}{27}-\frac{262}{27R}\right]\right)\right\}$$

[18] The definition of Q_τ underlying the development (32) gives it twice the value now conventional.

$$-e^{R/2}S'Q'Ei(-3R)+e^{-5R/2}S'\left(\frac{83R}{45}-\frac{256}{27}-\frac{46}{27R}\right)$$
$$-\frac{e^{-3R/2}}{45}\left(R^3+\frac{12R^2}{3}+\frac{60R}{9}+\frac{120}{27}\right)\Bigg] \tag{34}$$

where

$$Q=\frac{R^2}{5}+\frac{12R}{5}+12+\frac{24}{R}\,; \qquad S=e^{-R}(1+R+R^2/3)\,;$$
$$Q'=\frac{R^2}{5}-\frac{12R}{5}+12-\frac{24}{R}\,; \qquad S'=e^{R}(1-R+R^2/3)\,.$$

$C=0.577216=$ Euler's constant.

$K_2^{(2)}$ is reducible to the form

$$K_2^{(2)}=\frac{R^4}{3840}\int_1^\infty(\lambda^2-1)\Bigg(\lambda^2+\frac{1}{7}\Bigg\{(3\lambda+R)e^{-3\lambda R/2}$$
$$-\left(\frac{3\lambda^2-1}{2}\right)e^{-\lambda R/2}\Big[S'Ei\{-(\lambda+1)R\}$$
$$-SEi\{-(\lambda-1)R\}-Sln\left(\frac{\lambda+1}{\lambda-1}\right)\Big]-3e^{-\lambda R/2}S\Bigg\}d\lambda \tag{35}$$

The final integration has been performed graphically. $K_2^{(2)}$ turns out to be small compared with $K_2^{(0)}$.

The last integral to be evaluated is

$$K_4=\frac{1}{64\pi^2}\int\frac{e^{-(b_1+a_1/2)}}{r_{12}}a_1\sin\theta_1{}^a e^{-(b_2+a_2/2)}a_2\sin\theta_2{}^a e^{i(\phi_2-\phi_1)}dV \tag{36}$$

Using the expansion (32) again we see that all terms must integrate to zero in which ν differs from unity. We may therefore replace $1/r_{12}$ by

$$-\frac{2}{R}\sum_{\tau=1}^{\infty}(2\tau+1)\left(\frac{\Pi(\tau-1)}{\Pi(\tau+1)}\right)^2 P_\tau^{(1)}\binom{\lambda_1}{\lambda_2}Q_\tau^{(1)}\binom{\lambda_2}{\lambda_1}P_\tau^{(1)}(\mu_1)P_\tau^{(1)}(\mu_2)\cos(\phi_2-\phi_1)$$

Integrating with respect to ϕ_1 and ϕ_2 and introducing elliptic coordinates in (36) we obtain

$$K_4=-\frac{R^7}{(64)^2}\int d\lambda_1 d\lambda_2 d\mu_1 d\mu_2\sum_\tau\Bigg\{\frac{(2\tau+1)}{\tau^2(\tau+1)^2}e^{-(R/4)(3\lambda_1-\mu_1)}e^{-(R/4)(3\lambda_2-\mu_2)}$$
$$\times P_\tau^{(1)}\binom{\lambda_1}{\lambda_2}Q_\tau^{(1)}\binom{\lambda_2}{\lambda_1}P_\tau^{(1)}(\mu_1)P_\tau^{(1)}(\mu_2)$$
$$(\lambda_1^2-1)^{1/2}(1-\mu_1^2)^{1/2}(\lambda_2^2-1)^{1/2}(1-\mu_2^2)^{1/2}(\lambda_1^2-\mu_1^2)(\lambda_2^2-\mu_2^2)\Bigg\}.$$

By means of the relations

$$P_\tau^{(1)}(x)=(1-x^2)^{1/2}\frac{d}{dx}P_\tau(x) \qquad Q_\tau^{(1)}(x)=(1-x^2)^{1/2}\frac{d}{dx}Q_\tau(x)$$

we may eliminate all the radical signs. Let $\alpha_\tau(R)$ and $\beta_\tau(R)$ be defined by

$$\alpha_\tau(R)=\int_{-1}^{+1}e^{Rx/4}(1-x^2)\frac{d}{dx}P_\tau(x)dx\ ;$$

$$\beta_\tau(R)=\int_{-1}^{+1}e^{Rx/4}x^2(1-x^2)\frac{d}{dx}P_\tau(x)dx.$$

Then K_4 may be thrown into the form

$$K_4=\frac{R^7}{(64)^2}\int_1^\infty d\lambda_1\int_1^\infty d\lambda_2 e^{-3R(\lambda_1+\lambda_2)/4}(\lambda_1^2-1)(\lambda_2^2-1)\sum_\tau\left\{\frac{2\tau+1}{\tau^2(\tau+1)^2}(\lambda_1^2\alpha_\tau+\beta_\tau)(\lambda_2^2\alpha_\tau+\beta_\tau)\frac{d}{d\lambda}P_\tau\binom{\lambda_1}{\lambda_2}\frac{d}{d\lambda}Q_\tau\binom{\lambda_1}{\lambda_2}\right\}.$$

The integrand is symmetric with respect to the line $\lambda_1=\lambda_2$ and hence the integral is equal to twice the partial integral over the segment between the lines $\lambda_2=1$ and $\lambda_2=\lambda_1$. By means of the relation

$$(\lambda^2-1)\frac{d}{d\lambda}p_\tau(\lambda)=\frac{\tau(\tau+1)}{2\tau+1}[P_{\tau+1}(\lambda)-P_{\tau-1}(\lambda)]$$

we may then express K_4 in the form

$$K_4=-\frac{2R^7}{(64)^2}\int_1^\infty d\lambda_1\left\{e^{-3R\lambda_1/4}(\lambda_1^2-1)\sum_{\tau=1}^\infty\frac{(\lambda_1^2\alpha_\tau+\beta_\tau)}{\tau(\tau+1)}F_\tau(\lambda_1,R)\frac{d}{d\lambda_1}Q_\tau(\lambda_1)\right\} \quad (37)$$

where

$$F_\tau(\lambda_1,R)=\int_{+1}^{\lambda_1}e^{-3R\lambda_2/4}(\lambda_2^2\alpha_\tau+\beta_\tau)\{P_{\tau+1}(\lambda_2)-P_{\tau-1}(\lambda_2)\}d\lambda_2.$$

The functions $\alpha_\tau(R)$, $\beta_\tau(R)$, $F_\tau(\lambda_1, R)$ have been evaluated analytically but the formulas are somewhat cumbersome and are therefore not reproduced here. The final step of integrating with respect to λ_1 has been performed graphically. Fortunately the series in τ converges rapidly so two terms only need be considered.

Results

We have computed the numerical values of the integrals J_1, J_2, K_1, K_2, K_3, K_4 for four different values of the internuclear distance R. The results are given in Table I. The energy values H_9^9 etc. are expressed in volts by means of the reduction factor $e^2/a_0=27.08$ volts.

Fig. 1 shows graphically the four computed approximate theoretical potential energy curves together with approximate curves for the C and B

states derived from the experimental band spectrum data. The zero level for the graph is the energy of the dissociated atom pair which lies 16.925 volts below the zero level of Eqs. (20) to (23).

TABLE I.

R	g_9^2	g_{10}^2	J_1	J_2	K_1	K_2	K_3	K_4
1	0.136	1.529	0.969	0.926	0.2365	0.204	0.016	0.015
2	.163	.534	.696	.4945	.220	.123	.012	.010
3	.195	.348	.531	.224	.199	.063	.008	.006
4	.221	.288	.428	.091	.178	.028	.006	.002

R	H_9^9	H_{10}^{10}	H_{11}^{11}	H_{12}^{12}
		(volts above E_0)		
1	2.25	25.26	1.16	25.6
2	−1.06	7.42	−1.81	7.63
3	−1.08	2.49	−1.68	2.65
4	−0.596	0.812	−0.894	1.06
	(S^E, S^N)	(S^E, A^N)	(A^E, S^N)	(A^E, A^N)

The energy of dissociation and the moment of inertia serve to determine ordinate and abscissa R_0 of the minimum point on each of the "empirical" curves while the vibrational frequency and the variation of the moment of inertia with vibrational quantum number may be used to evaluate the second and third derivatives of the potential energy with respect to R at the minimum point.[19] The attractive force between the atoms at large distances should vary as R^{-7}. Hence the best estimate which we can make regarding the form of the actual potential energy curve for any given molecular state is obtained by using a function of the form

$$V(R) = \sum_{n=6}^{9} a_n / R^n \tag{38}$$

[19] The values of the heat of dissociation (indirect calculation) given by Birge[8] for the B and C states are 3.37 volts and 2.27 volts respectively. These are increased by the equivalent of a half quantum of vibrational energy in passing from the old to the new mechanics. Using 14.5 volts as the energy for $R=\infty$, we obtain in this way

$$V(R_0)_B = 14.5 - 3.45 = 11.05 \text{ volts}$$
$$V(R_0)_C = 14.5 - 2.42 = 12.08 \text{ volts}$$

From the vibrational frequencies given by Birge we compute

$$V''(R_0)_B = 0.919 \qquad V''(R_0)_C = 2.98$$

Finally $V''''(R_0)$ may be determined from the variation of the constant $B = h/(8\pi^2 IC)$ with the vibrational quantum number. The formula

$$V''' = V''\left[\frac{\omega_0}{2B_0^2}\left(\frac{dB}{dn}\right)_{n=0} - 3\right]\frac{a_0}{R_0}$$

is to be used. It yields

$$V''(R_0)_B = -1.48; \qquad V''(R_0)_C = 6.95.$$

The equilibrium internuclear distances themselves are

$$(R_0)_B = 2.45; \qquad (R_0)_C = 1.99$$

the unit as always being $a_0 = 0.532 \times 10^{-8}$ cm.

where the a's are determined to fit the known heat of dissociation and to give the correct values to V and its derivatives at the point $R = R_0$. Curves C and B are graphs of such empirical formulas. A comparison of H_9^9 and C_2 shows that the former is in reasonable harmony with our experimental information. The discrepancy for small values of R is not surprising since the approximate wave-functions used must be very inaccurate for the smaller internuclear distances

In addition to B and C there is a $2P$ level reported by Richardson[20] and classified by him as a triplet state. The location of this level has been determined by a Rydberg series into which it fits, there being no known direct combination with the normal state. As the bands associated with this state have not been completely analyzed, the empirical data are somewhat uncertain and we have plotted only a fragment of the empirical potential energy curve (D). Clearly this state is to be correlated with our energy curve for H_{11}^{11}. The agreement is about the same as for the C state.

On the whole the comparison of the H_9^9 and H_{11}^{11} values with the corresponding experimental data seems to justify the conclusion that all four of the theoretical potential energy curves are qualitatively correct and that the remaining P states (H_{10}^{10} and H_{12}^{12}) are both of a type which does not lead to the formation of a stable molecule.

These results shed some light on London's theory of non-polar valence.[7] Two *normal* H atoms can react only in two ways, as Heitler and London have shown. In first approximation the corresponding wave functions in our notation are

$$\psi_S = \psi_1^a \psi_2^b + \psi_2^a \psi_1^b \qquad (S^E S^N)$$

$$\psi_A = \psi_1^a \psi_2^b - \psi_2^a \psi_1^b \qquad (A^E A^N)$$

Here ψ_S is symmetric with respect to both of the transformations (E) and (N) and ψ_A is antisymmetric with respect to both. Hybrid symmetries like that of our function U_{10} drop out because both electrons have the same quantum number. Only the symmetric mode of interaction leads to molecular formation and in his first paper on valence theory London infers that symmetry in the coordinates of the valence electron is the characteristic feature of the homopolar bond. This means that when a non-polar molecule is formed by two atoms each of which has a single valence electron a singlet state must result, triplet type interactions leading to repulsion. Our computation and the empirical data show that both singlet and triplet states may lead to the formation of excited molecules, the triplet states being more stable energetically than corresponding singlet states with the same symmetry

[20] O. W. Richardson, Proc. Roy. Soc. **A114,** 643 (1927). Cf. also Birge (Ref. 8 above) and Richardson, Nature **121,** 320 (1928).

[21] It is well known that in atoms with two valence electrons each triplet level lies below the corresponding singlet level. If the singlet-triplet difference always has the same sign for molecules, and if it decreases monatonically as R increases from 0 to infinity, a triplet level must always be more stable than a singlet level similar to it except for electron symmetry.

with respect to the nuclei[21] (i.e., with respect to the transformation z_1, $z_2 \rightarrow -z_1, -z_2$). It therefore appears that in the case of hydrogen symmetry in the nuclei has a more important effect on molecular formation than symmetry in the electrons. The reason for this importance is that antisymmetry in the nuclei introduces a "node" including all points for which $z_1 = z_2 = 0$ and leading to an increase in the azimuthal quantum number of one of the electrons in the limit when the nuclei are brought together and the wave function becomes helium-like. This "promotion" and consequent increase in energy for small values of R must tend to produce repulsion and since the removal of degeneracy is generally accompanied by the lifting of half of the sublevels coming from any parent level and a corresponding depression of the remaining sublevels, it is plausible to suppose that the absence of promotion in the case of states with the symmetry S^N should produce attraction and molecular formation. Our conclusion confirms the suggestion made by London in his second paper on valence theory to account for the triplet levels found by Ritschl and Villars in the band spectra of Na_2 and K_2.

The success of London's theory in describing the facts regarding the *normal* states of molecules must then be due to the fact that in such states the symmetry of the wave function with respect to an interchange of the coordinates of the valence electrons determines the presence or absence of a node between the nuclei. We have made no detailed examination of this question, but surmise that the occurrence of such states as U_{11} above which are antisymmetric in the coordinates of the valence electrons but lack the node between the nuclei is dependent on the fact that two atoms which make up the molecule are identical, but dissociate into different states of excitation.

The B State

It would be natural to infer from our results that in the case of diatomic molecules consisting of identical atoms symmetry in the nuclei is always the crucial element in producing attraction. Such a generalization strikes a snag immediately, however, in the B state of the hydrogen molecule which must have the symmetry $S^E A^N$ to account for its union with the normal state of the molecule to form a band system. From the discussion above it will be clear that both types of symmetry tend to produce repulsion. Nevertheless, the B state is actually the most stable energetically of the known two quantum states of H_2.

The most probable explanation of this puzzling situation lies in the fact that the two quantum molecular S states ($\sigma_k = 0$) have in zero approximation an additional type of degeneracy not present in the case of the P states ($\sigma_k = \pm 1$). There are two two quantum molecular S states with the symmetry $S^E A^N$ of the B state. The wave functions in zero approximation are mixtures of U_2 and U_5 and the energy difference given by (14) is $[(H_2^2 - H_5^5)^2 + 4(H_5^2)^2]^{1/2}$. To account for the stability of the B state we must suppose that this energy difference for moderate values of R is quite large compared with the energy differences due to the symmetry in the electrons

and in the nuclei.[22] The companion state to B with the same symmetry will then be strongly repulsive in type.

An alternative suggestion regarding the B state due to Pauling[23] attributes this energy level to a union of H^+ and H^- ions. In other words, he supposes that the B state does not dissociate adiabatically into a normal H atom and a two quantum H atom, but into H^+ and H^- ions. This hypothesis is compatible with the fact that the B state is of the S type and with its symmetry. It accounts for the fact that the atoms in the B state begin to attract each other at extraordinarily large interatomic distances. The proposal does not recommend itself to us, however, since it leads to a value of the dissociation energy too large for satisfactory agreement with the experimental vibrational energy data. (This fact was first called to our attention by Professor R. S. Mulliken.) The energy of the H^- ion is not exactly known and it may be that the ion does not exist. We can hardly go far wrong, however, if we assume that the binding energy of the second electron is zero. In that case the energy of the dissociation products of the B state of the molecule must be three volts higher according to Pauling's hypothesis than according to our own assumption (borrowed from Dieke and Hopfield)[9], that the B state dissociates adiabatically into a normal atom and a two quantum excited atom. The vibrational energy data extrapolated by Birge[8] yield 3.41 volts as the energy of dissociation, whereas the value computed on the basis of the second hypothesis above from the more accurately known vibrational data for the normal state is 3.37 volts. It is extremely unlikely that this extrapolation can be in error by the three volts required to make it agree with Pauling's suggestion. Moreover, a consideration of the nodes of the wave function of any molecular state X dissociating into ions suggests that these nodes must be numerous (Cf. as a one dimensional analogy, Hund, Zeits. f. Physik 40, 748, Figs. 3 and 4). If so, X should pass into a high quantum state of He when the nuclei are brought together. Hence the attraction between the atoms at large distances due to the Coulomb forces would soon be counterbalanced with decreasing R by the repulsive action due to multiple promotion of the electrons. It would therefore be difficult to account for such a low energy at intermediate values of R as that associated with the B state.

In view of these facts regarding the B state it appears that neither of the two types of symmetry S^E and S^N is a universal characteristic of the wave functions of stable diatomic molecules. On the other hand there are as yet no definite known exceptions to the less stringent rule that molecular formation always involves the removal of some type of degeneracy characteristic of the atom pair when completely separated. The authors wish to express

[22] The choice of the coefficients c_2 and c_4 in the expression for ψ

$$\psi = c_2 U_2 + c_4 U_4 \qquad \text{(A)}$$

is readily shown to be that which makes the energy of the resulting state either a maximum or a minimum. Hence, if the variation in the energy integral due to varying the ratio c_2/c_4 is large, one of the two states of type $(S^E A^N)$ will form a stable molecule.

[23] L. Pauling, Chem. Reviews **5**, 204 (1928).

their great appreciation for the assistance of Dr. V. Guillemin in checking the computations.*

Note added at reading of proof. Since writing the above paragraphs on the *B* state we have come to the conclusion that the argument needs modification. If one tries to build up wave-functions for the neutral H_2 molecule from the wave functions of the molecule-ion, it is at once apparent that a suitable combination of the functions for the two lowest ionic terms will yield rough approximations to the lowest energy levels of the polar type of neutral molecule. As one of the molecular ion wave functions to be used has a single node while the other has none, it will be clear that the approximate terms for the polar type neutral molecule will *not* undergo multiple promotion when the nuclei are brought together.

In order to bring this fact into line with the argument regarding the nodes given above, it is necessary to recall Hund's discussion of the possible crossing of terms during the adiabatic variation of a parameter such as the internuclear distance R. (Zeits. f. Physik **40**, 751–3, 1927). He observes that we may expect that in many cases an approximate computation will suggest a crossing of terms where a more rigorous treatment would show that the crossing does not actually occur.

The situation will be made clear by the following analytical treatment. Let ψ_1 and ψ_2 be two approximate wave functions with approximate energy values $E_1(R)$ and $E_2(R)$. Let the terms cross at $R=R_1$ and to be specific we assume that E_1 lies above E_2 when $R>R_1$. We shall suppose that $E_1=\int\bar{\psi}_1 H\psi_1 dv$ while $E_2=\int\bar{\psi}_2 H\psi_2 dv$. If there are no other approximate solutions having energies close to E_1 and E_2 at $R=R_1$, we may assume that in this neighborhood to a close approximation the actual wave functions will be linear combinations of ψ_1 and ψ_2. Thus we assume

$$\psi=c_1\psi_1+c_2\psi_2. \tag{a}$$

Then by equation (7) above

$$c_1(E_1-E)+c_2H_2^1=0; \qquad c_1H_1^2+c_2(E_2-E)=0. \tag{b}$$

If the energy operator H is real, the conjugate integrals H_2^1 and H_1^2 must be equal. Then E is a root of the equation

$$(E_1-E)(E_2-E)-(H_2^1)^2=0.$$

The two roots are

$$\begin{aligned} E^+&=\frac{E_1+E_2}{2}+\left[(H_2^1)^2+\frac{(E_2-E_1)^2}{4}\right]^{1/2} \\ E^-&=\frac{E_1+E_2}{2}-\left[(H_2^1)^2+\frac{(E_2-E_1)^2}{4}\right]^{1/2} \end{aligned} \tag{c}$$

* The article by *Hylleraas* (Zeits. f. Physik **51**, 150, 1928) describing a computation of the two-quantum S states of H_2 came to hand after the present paper was finished. Hylleraas comes to the same conclusion as that reached by us in that he finds that symmetry in the nuclei is more important than symmetry in the electrons in its influence on molecular binding. Unfortunately his computation is, in our opinion, incorrect as he neglects the interaction between the states $\psi(2, 0, 0)$ and $\psi(2, 1, 0)$ (our notation) in molecular formation. Unless this interaction is taken into account, the characteristics of the *B* state are hardly explicable.

We assume that $H_2^1(R)$ is small compared with $E_1(R)$ and $E_2(R)$ in the neighborhood of $R=R_1$. Then equations (c) show that E^+ approximates to E_1 when $R-R_1$ has large positive value, but to E_2 when $R-R_1$ has large negative value. Similarly E^- approximates to E_2 on the one side of $R=R_1$ and to E_1 on the other. If H_2^1 does not vanish, there is no crossing and the separation of the levels at $R=R_1$ is $2H_2^1(R_1)$. If H_2^1 is rigorously zero, we may, if we like, say that the terms cross. If $H_2^1(R_1)$ is very small, the energy level curves for E^+ and E^- will come very close to one another at $R=R_1$ and will bend sharply near this point, but if H_2^1 is large, the two curves will apparently repel one another when still far apart and the bend near $R=R_1$ will be less abrupt. Finally, if there is no crossing point but the term values E_1 and E_2 merely approach one another at $R=R_1$, the interaction will cause a depression of the lower one and an elevation of the upper one is if due to mutual repulsion.

If H_2^1 does not vanish, the substitution of the value of E^+ given in (c) into either of the equations (b) leads to the relation

$$c_1^+/_2^+c = x-(1+x^2)_2^1 \qquad \text{(d)}$$

where $x=(E_2-E_1)/2H_2^1$. From equation (d) we see that when x is large and positive (E^+-E_2 small) c_1^+/c_2^+ is sensibly equal to zero, while if x has a large negative value c_1^+/c_2^+ becomes infinite. More generally, if E^+ or E^- differs but little from one of the approximate energy values E_1 and E_2 in a certain range of R values, the actual wave-function will differ but little from the corresponding approximate function. At the apparent crossing point $R=R_1$ each of the rigorous wave functions is composed of equal parts of ψ_1 and ψ_2.

Although the integral $H_2^1(\int\dot{\psi}^1 H\psi_2 dv)$ always vanishes for two exact solutions of the wave equation which satisfy the boundary conditions, the chance that it will vanish rigorously for two approximate solutions is infinitesimal unless the symmetry of the solutions is different. Hence we conclude that if the approximate term for the polar type of neutral molecule having the symmetry $S^E A^N$ of the B state crosses the two approximate two quantum S terms of the same symmetry which dissociate into neutral atoms, this crossing will not occur when a more rigorous solution of the problem is worked out. In all probability, therefore, the B state would dissociate adiabatically into two neutral atoms. On the other hand, it is also probable that the wave function of the B has distinctly polar characteristics which are responsible for the depth of its potential energy minimum. Thus in an important physical sense we are led to accept Pauling's interpretation of the B state as one with ionic binding.

The two quantum P states of the molecule, however, would not be similarly affected by polar characteristics since their symmetry would cause the interaction integral with the lowest polar states to vanish (cf. p. 520 above).

This supplementary note originated in a discussion of the term-crossing problem with Professor Slater, to whom we are greatly indebted.

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December, 1928.

SPECTRAL RELATIONS BETWEEN CERTAIN ISO-ELECTRONIC SYSTEMS AND SEQUENCES. PART I; CA I, Sc II, Ti III, V IV AND Cr V

By H. E. White

Abstract

The spectra of trebly ionized vanadium, V IV, and quadruply ionized chromium, Cr V.—The neutral atoms of vanadium and chromium contain five valence electrons, $3d^34s^2$, and six valence electrons, $3d^54s$, respectively. The removal of three electrons, $3d4s^2$, from vanadium and four electrons, $3d^34s$, from chromium yields two iso-electronic systems, V IV and Cr V, the lowest energy levels of which arise from the two remaining electrons, $3d^2$. The spectra from these two systems should resemble very closely the spectra of neutral calcium, singly ionized scandium, and doubly ionized titanium. Extrapolations from the already known data of Ca I, Sc II, and Ti III, to V IV and Cr V have led to the identification of some thirty energy levels in both triply ionized vanadium and quadruply ionized chromium. The strongest lines in these spectra arise from combinations between ^3P, $^3D'$, ^3F, ^1P, $^1D'$, ^1F $(3d4p)$ and ^3D, $^1D(3d4s)$, and ^1S, $^3P'$, ^1D, $^3F'$, $^1G(3d^2)$.

The irregular doublet law and the Moseley law.—Following the irregular doublet law, the radiated frequencies resulting from transitions between the terms arising from $3d4p$ and $3d4s$ as well as from transitions between the terms arising from $3d4d$ and $3d4p$ in going from element to element are displaced to higher and higher frequencies by very nearly a constant frequency interval. The combination of ordinary energy level diagrams with a Moseley diagram brings out a number of interesting relations between the iso-electronic systems K I, Ca II, Sc III, Ti IV and V V, and the iso-electronic systems Ca I, Sc II, Ti III, V IV and Cr V. The Moseley diagram and the irregular doublet law served admirably in determining the approximate positions of the various singlet and triplet levels as well as the approximate location in the spectrum of the radiated frequencies.

Landé interval rule; Hund's rule.—The triplet term separations follow fairly well the Landé interval rule. In general Hund's rule is valid for low lying terms in each spectrum. One violation, however, in the middle terms should be mentioned namely; the $^1D_2$ term arising from the electron configuration $3d4p$ lies deeper than the triplet terms. The ionization potentials, that is the voltage necessary to remove one $3d$ electron from the normal state $^3F_2'(3d^2)$ of V IV and Cr V, to the normal state $^2D_2(3d)$ of the once more ionized atoms are determined at about 48.3 volts and 72.8 volts respectively.

STARTING with any element in the periodic table a sequence of iso-electronic systems is obtained by removing one, two, three, · · · electrons from the first, second, third, · · · succeeding elements in the periodic table. For example, neutral potassium contains nineteen electrons, eighteen of which form what are called "closed shells." The succeeding elements calcium, scandium, titanium, vanadium, etc., are made iso-electronic (that is, having the same number of electrons) with potassium by removing one electron from calcium, two electrons from scandium, three electrons from titanium, four electrons from vanadium, etc. The atoms so defined form the sequence of iso-electronic systems K I, Ca II, Sc III, Ti IV, V V, etc. The known spectro-

scopic terms or energy levels for the first seven of these atomic systems,[1] being doublet in character, are attributed to the one remaining *valence* electron.

By placing the ordinary energy-level diagrams of each of these spectra side by side, in the order in which they appear in the sequence, certain interesting relations become apparent.

A Moseley diagram plotted for the same energy levels brings out still other regularities. An attempt to combine these two types of diagram has resulted in Fig. 1. In this diagram the square root of the term values is plotted against the atomic number. Two relations, brought out by the diagram, may be mentioned, first the crossing of the 3^2D terms over the 4^2P and 4^2S terms which indicates *an increased binding of a 3d electron over a 4p and*

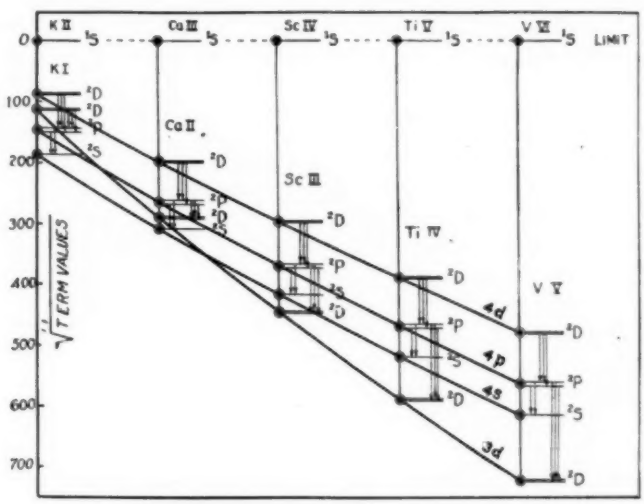

Fig. 1. Energy levels and the Moseley law.

a 4s electron, and second the *parallelism existing between the lines 4s, 4p, and 4d*. This latter regularity is a result of the so-called *irregular doublet law*.

Extrapolations from the known spectroscopic data of neutral calcium,[2] singly ionized scandium,[3] and doubly ionized titanium,[4] the first three elements in the sequence of iso-electronic systems Ca I, Sc II, Ti III, V IV, Cr V, etc., have led to the identification of some thirty of the lower energy levels in triply ionized vanadium and quadruply ionized chromium.

The neutral atoms of vanadium and chromium contain five valence electrons, $3d^34s^2$, and six valence electrons, $3d^54s$, respectively. The removal of three electrons, $3d4s^2$, from vanadium and four electrons, $3d^34s$, from chromium give the normal configuration of V IV and Cr V as $3d^2$. Above the

[1] Gibbs and White, Proc. Nat. Acad. Sci. **12,** 448 (1926); **12,** 675 (1926).
[2] Russell and Saunders, Astrophys. J. **61,** 38 (1925).
[3] Russell and Meggers, Bureau of Standards, Sci. Papers **22,** No. 558, (1927).
[4] Russell and Lang, Astrophys. J. **66,** 167 (1927).

^1S, $^3P'$, ^1D, $^3F'$, and ^1G terms arising from $3d^2$ are the metastable levels ^1D and ^3D of $3d4s$. Still higher are found the ^1P, $^1D'$, ^1F, ^3P, $^3D'$ and ^3F terms of $3d4p$ which combine strongly with those of $3d^2$ and $3d4s$.

Contrary to Hund's rule that in any electron configuration the terms with largest R, L, and J values should lie deepest, the $^1D_2$ term in Sc II, Ti III, V IV and Cr V lies deeper than all other terms of the $3d4p$ configuration. The locating of this low $^1D_2$ term in V IV confirms the assignment of the corresponding $^1D_2$ term in Sc II made by Russell and Meggers[3] and of the corresponding $^1D_2$ term in Ti III made by Russell and Lang.[4] The relative shifting of the energy levels arising from the electron configuration $3d4p$ is shown graphically in Fig. 2 for all five elements Ca I, Sc II, Ti III, V IV and

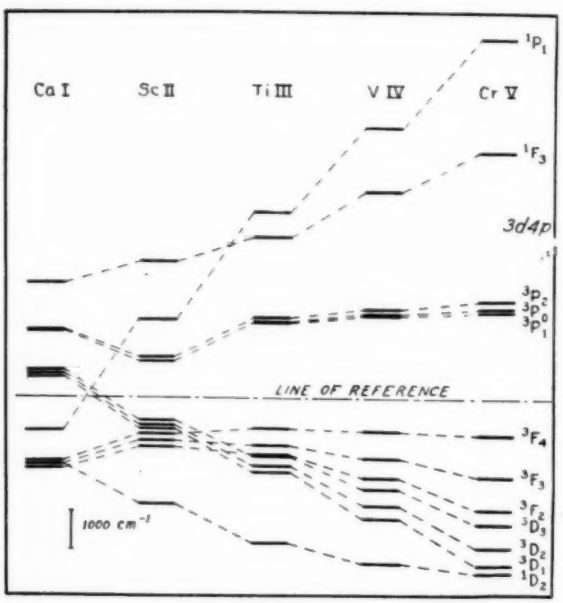

Fig. 2. Relative energy levels.

Cr V. Following a scheme similar to the one used by Mack, Laporte and Lang[5] each set of energy levels has been plotted with reference to the line through the center of the figure. The *line of reference* for each set of levels is a weighted mean, each term being weighted in proportion to its J value. The selection of this line of reference from which to plot each set of levels is purely arbitrary for nearly any one of the terms would serve equally well. Intercombinations in Cr V are so weak that the positions of the singlet terms with respect to the triplet terms are not certain. From the shifts shown in Fig. 2, however, it is to be expected that in Mn VI the $^3D_1$ term will be deepest.

[5] Mack, Laporte and Lang, Phys. Rev. **31**, 748 (1928).

In a previous report on this sequence of iso-electronic systems Gibbs and White[6] have shown that certain transitions follow very closely the *irregular* doublet law. In short the irregular doublet law means that in any electron transition which involves no change in total quantum number the radiated

TABLE I. *Irregular doublet law.*

Element	$3d4p$ to $3d4s$ $^3D_3-{}^3F_4$	$\Delta\nu$	$^1D_2-{}^1D_2'$	$\Delta\nu$	$3d4d$ to $3d4p$ $^3F_4-{}^3G_5$	$\Delta\nu$
Ca I	15526		13986		(13974)	
		12137		9554		(18640)
Sc II	27663		23540		32614	
		12070		9954		18700
Ti III	39733		33494		51314	
		11838		10578		18782
V IV	51571		44072		70096	
		11733		10865		18902
Cr V	63304		54937		88998	

frequencies in going from one element to the next are displaced to higher and higher frequencies by very nearly a constant frequency interval. In this sequence two such sets of radiated frequencies have been found, first, the set of lines arising from the electron transition $3d4p$ to $3d4s$, and second, the set of lines arising from the electron transition $3d4d$ to $3d4p$. Examples of

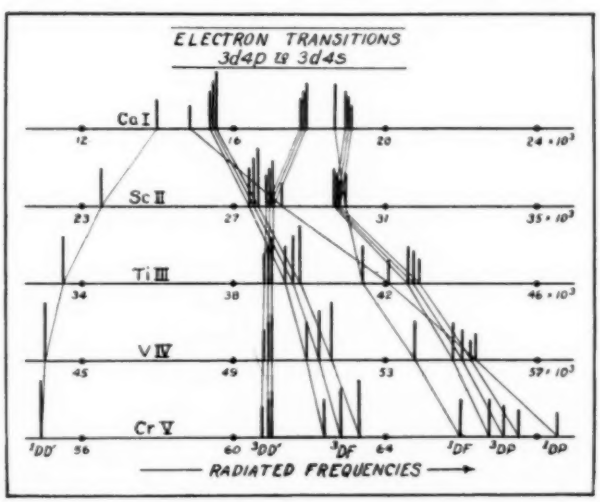

Fig. 3. Regular displacement of frequencies.

this linear relation are given in Table I for the lines $^3D_3-{}^3F_4$ and $^1D_2-{}^1D_2'$ representing the first set of transitions and for the line $^3F_4-{}^3G_5$ representing the second set of transitions. None of the terms arising from the electron configuration $3d4d$ has yet been determined for Ca I, however, an extrapola-

[6] Gibbs and White, Phys. Rev. **29**, 426 (1927).

tion by means of the last column of Table III locates the frequency of the $^3F_4-{}^3G_5$ transition not far from $\nu=13974$ cm^{-1}.

The almost linear displacement of frequency with atomic number for the transitions $3d4p$ to $3d4s$ is shown graphically in Fig. 3 for the singlets as well as the strongest lines of the triplets. In this figure each frequency scale, although the same for all elements, has been displaced to the left of the one just preceding it by 11000 cm^{-1}. This type of diagram shows not only the successive displacement of each group of lines toward the violet by about 11000 cm^{-1} but also the variation ($\Delta\nu$) in this displacement for each line

TABLE II. *Relative term values of V IV.*

Config. (Limit)	Term	Value	Combinations	$(\nu)^{1/2}$	Config. (Limit)	Term	Value	Combinations	$(\nu)^{1/2}$
	a^3F_2'	000	^3F, $^3D'$			$^3D_2'$	146426		
		318					425		
	a^3F_3'	318				$^3D_3'$	146851		494
		412							
	a^3F_4'	730		625		$^3F_2$	147133	$^3P'$, ^3D	
							520	a^3F', ^1D	
	a^1D_2	11658	^3P, ^1P	616		$^3F_3$	147653		
			$^1D'$, ^1F				712		
$3d^2$	$^3P_0'$	13121	^3P, $^3D'$		$3d4p$	$^3F_4$	148365		493
$(3d)$		117	^3F		$(3d)$				
	$^3P_1'$	13238				$^3P_1$	151424	^3D, $^3P'$	
		215					−22	a^1D_2	
	$^3P_2'$	13453		615		$^3P_0$	151446		
							140		
	$^1G_4$	19087	^1F	610		$^3P_2$	151564		490
	$^1S_0$	20091	^1P	609		$^1F_3$	154618	a^1D, ^1G	487
								b^1D	
						$^1P_1$	156265	^1S,a^1D	485
	$^3D_1$	96195	^3P, $^3D'$					b^1D	
		215	^3F, $^1D'$			$^3G_3$	217835	^3F	
	$^3D_2$	96410					262		
$3d4s$		385				$^3G_4$	218097		
$(3d)$	$^3D_3$	96795		543			364		
	b^1D_2	100902	^3F, ^1P	539	$3d4d$	$^3G_5$	218461		416
			$^1D'$, ^1F		$(3d)$				
						b^3F_2'	223510	^3F, ^3D	
	$^1D_2'$	144974	^3D, a^1D	496			323		
			b^1D			b^3F_3'	223833		
	$^3D_1'$	146116	a^3F', $^3P'$				430		
		310				b^3F_4'	224263		409

separately. Combinations between $3d4p$ and $3d4s$ in both V IV and Cr V show that our previous assignments[6] of $^3P_{2,1,0}$ for V IV and $^3F_{4,3,2}$ for Cr V were not correct. This error was due primarily to a lack of sufficient data in the vacuum region of the spectrum. The spectra of V IV and Cr V given in this report were measured from plates taken with a vacuum spectrograph now available in this laboratory.

The relative term values of V IV and Cr V are given in Tables II and III, the lowest term in each spectrum $a^3F_2'(3d^2)$ being taken as zero. The values

of $(\nu)^{1/2}$ given in the fifth and tenth columns of Tables II and III are taken with respect to the limit toward which each term converges in series, namely, the $^2D_3$ term of the once more ionized atoms. The method used to obtain these limiting term values is by suitable extrapolations on a Moseley diagram, similar to that shown in Fig. 1, from Ca I, Sc II, Ti III where the limits are known with considerable accuracy.

TABLE III. *Relative term values of Cr V*

Config. (Limit)	Terms	Values	Combinations	$\nu^{1/2}$
	a^3F_2'	000	$^3F, ^3D'$	
		500		
	a^3F_3'	500		
		637		
	a^3F_4'	1137		767
	a^1D_2	14921	$^1P, ^1D'$ ^1F	758
$3d^2$ (3d)	$^3P_0'$	15470	$^3D', ^3P$	
		208		
	$^3P_1'$	15678		
		368		
	$^3P_2'$	16046		757
	$^1G_4$	23237	^1F	752
	$^1S_0$	25296	^1P	751
	$^3D_1$	167159	$^3P, ^3D'$	
		314	$^3F, ^1D'$	
	$^3D_2$	167473		
3d4s		598		
	$^3D_3$	168071		
(3d)				649
	b^1D_2	172908	$^1P, ^1D'$ ^1F	645

Config. (Limit)	Terms	Values	Combinations	$\nu^{1/2}$
	$^1D_2'$	227845	a^1D, b^1D ^3D	601
	$^3D_1$	227987	$^3D, a^3F'$	
		487	$^3P'$	
	$^3D_2$	228474		
		631		
	$^3D_3$	229105		600
	$^3F_2$	229537	$^3D, a^3F'$	
3d4p		762	^3G	
(3d)	$^3F_3$	230299		
		1076		
	$^3F_4$	231375		598
	$^3P_0$	234651	$^3D_3, ^3P'$	
		−55		
	$^3P_1$	234596		
		230		
	$^3P_2$	234826		595
	$^1F_3$	238740	a^1D, b^1D ^1G	592
	$^1P_1$	241624	a^1D, b^1D ^1S	589
3d4d (3d)	$^3G_3$	319295	^3F	
	$^3G_4$	319780		
	$^3G_5$	320373		518

Triplet separations for three of the electron configurations of Ca I, Sc II, Ti III, V IV, and Cr V are given in Table IV. A careful study of Table IV shows that with the increasing term separations Landé's interval rule is in general in operation.

TABLE IV. *Term separations*

	$3d^2$		$3d^2$		$3d4p$		$3d4s$	
	a^3F_4'	a^3F_3' a^3F_2'	$^3P_2'$	$^3P_1'$ $^3P_0'$	$^3D_3'$	$^3D_2'$ $^3D_1'$	$^3D_3$	$^3D_2$ $^3D_1$
Ca I	—	—	—	—	40	25	22	14
Sc II	104	21	53	27	140	103	110	68
Ti III	238	184	118	67	257	167	227	134
V IV	412	318	215	117	425	310	385	215
Cr V	637	500	368	208	631	487	598	314

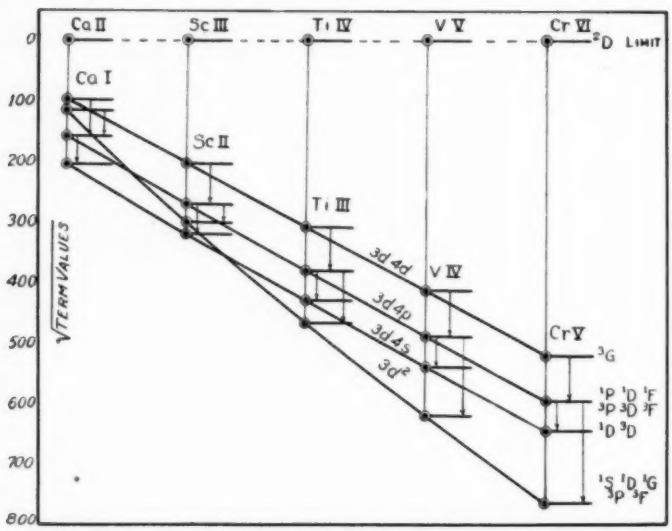

Fig. 4. Energy levels and the Moseley law.

TABLE V. *Triply ionized vanadium*

$\lambda_{vac.}$	Int.	ν	Designation	$\lambda_{vac.}$	Int.	ν	Designation
2269.00	100	44072.3	$b^1D_2-{}^1D_2'$	752.59	8	132874	$^3P_1'-{}^3D_1'$
2163.18	1	46228.2	$b^1D_2-{}^3F_2$	752.06	10	132968	$^3P_2'-{}^3D_2'$
2059.18	1	48563.0	$^3D_2-{}^1D_2'$	751.92	10	132993	$^3P_0'-{}^3D_1'$
2050.04	1	48779.5	$^3D_1-{}^1D_2'$	750.85	12	133183	$^3P_1'-{}^3D_2'$
2014.83	50	49632.0	$^3D_3-{}^3D_2'$	750.10	30	133316	$a^1D_2-{}^1D_2'$
2011.80	25	49706.7	$^3D_2-{}^3D_1'$	749.66	15	133393	$^3P_2'-{}^3D_3'$
2003.12	50	49922.1	$^3D_1-{}^3D_1'$	746.88	5	133890	$^3P_1'-{}^3F_2$
1999.32	60	50017.0	$^3D_2-{}^3D_2'$	745.21	6	134191	$^3P_2'-{}^3F_3$
1997.74	80	50056.6	$^3D_3-{}^3D_3'$	737.84	100	135530	$^1G_4-{}^1F_3$
1990.75	30	50232.3	$^3D_1-{}^3D_2'$	734.36	8	136173	$^1S_0-{}^1P_1$
1986.54	0	50338.8	$^3D_3-{}^3F_2$	724.79	20	137971	$^3P_2'-{}^3P_1$
1982.49	30	50441.6	$^3D_2-{}^3D_3'$	724.06	30	138109	$^3P_2'-{}^3P_2$
1971.47	10	50723.6	$^3D_2-{}^3F_2$	723.65	20	138188	$^3P_1'-{}^3P_1$
1966.25	5	50858.2	$^3D_3-{}^3F_3$	723.54	15	138208	$^3P_1'-{}^3P_0$
1963.13	70	50939.0	$^3D_1-{}^3F_2$	723.04	15	138304	$^3P_0'-{}^3P_1$
1951.48	80	51243.1	$^3D_2-{}^3F_3$	722.94	20	138324	$^3P_1'-{}^3P_2$
1939.07	100	51571.1	$^3D_3-{}^3F_4$	715.46	1	139770	$a^1D_2-{}^3P_1$
1861.56	60	53718.4	$b^1D_2-{}^1F_3$	699.50	15	142959	$a^1D_2-{}^1F_3$
1825.85	50	54769.1	$^3D_3-{}^3P_2$	691.54	30	144605	$a^1D_2-{}^1P_1$
1817.72	30	55014.0	$^3D_2-{}^3P_1$	684.44	50	146104	$a^3F_3'-{}^3D_2'$
1813.10	8	55154.1	$^3D_2-{}^3P_2$	684.38	80	146117	$a^3F_4'-{}^3D_3'$
1810.61	6	55230.0	$^3D_1-{}^3P_1$	684.38		146117	$a^3F_2'-{}^3D_1'$
1809.88	15	55252.3	$^3D_1-{}^3P_0$	682.94	20	146426	$a^3F_2'-{}^3D_2'$
1806.22	40	55364.2	$b^1D_2-{}^1P_1$	682.46	20	146529	$a^3F_3'-{}^3D_3'$
1434.10	2	69730.1	$^3F_4-{}^3G_4$	681.13	25	146815	$a^3F_3'-{}^3F_2$
1426.62	17	70095.8	$^3F_4-{}^3G_5$	680.64	20	146921	$a^3F_4'-{}^3F_3$
1424.88	2	70181.3	$^3F_3-{}^3G_3$	679.65	25	147134	$a^3F_2'-{}^3F_2$
1419.56	15	70444.3	$^3F_3-{}^3G_4$	678.72	35	147335	$a^3F_3'-{}^3F_3$
1414.39	12	70701.8	$^3F_2-{}^3G_3$	677.35	50	147635	$a^3F_4'-{}^3F_4$
1317.56	4	75897.8	$^3F_4-b^3F_4'$	677.26	10	147653	$a^3F_2'-{}^3F_3$
1312.68	4	76180.0	$^3F_3-b^3F_3'$	675.48	10	148043	$a^3F_3'-{}^3F_4$
1309.29	4	76377.3	$^3F_2-b^3F^2'$				
1291.73	4	77415.5	$^3D_3-b^3F_4'$				

The same type of Moseley diagram may be drawn for the singlets and triplets of this sequence of iso-electronic systems Ca I, Sc II, Ti III, etc. as was drawn in Fig. 1 for the doublets of the previous sequence. In Fig. 4, a single level is drawn to represent all of the levels arising from each configuration.

Although the points plotted are terms involving the largest R, K, and J, values from each electron configuration, the points for all the terms in this configuration would lie within the range covered by the circle. A single arrow is drawn therefore to represent all of the observed radiated frequencies. A comparison of the diagrams for singlets and triplets, Fig. 4, with that for

TABLE VI. *Quadruply ionized chromium*

$\lambda_{vac.}$	Int.	ν	Designation	$\lambda_{vac.}$	Int.	ν	Designation
1820.28	60	54936.6	$b^1D_2-{}^1D_2'$	471.03	4?	212301	$^3P_1'-{}^3D_1'$
1656.42	1	60371.2	$^3D_2-{}^1D_2'$	470.75	5	212428	$^3P_2'-{}^3D_2'$
1655.55	25	60402.9	$^3D_3-{}^3D_2'$	470.56	10	212513	$^3P_0'-{}^3D_1'$
1652.52	20	60513.6	$^3D_2-{}^3D_1'$	469.95	20	212788	$^3P_1'-{}^3D_2'$
1647.71	0	60690.1	$^3D_1-{}^1D_2'$	469.65	30	212924	$a^1D_2-{}^1D_2'$
1644.00	40	60827.2	$^3D_1-{}^3D_1'$	469.34	30	213065	$^3P_2'-{}^3D_3'$
1639.35	50	60999.8	$^3D_2-{}^3D_2'$	464.03	100	215503	$^1G_4-{}^1F_3$
1638.42	70	61034.4	$^3D_3-{}^3D_3'$	462.26	5	216328	$^1S_0-{}^1P_1$
1630.91	10	61315.5	$^3D_1-{}^3D_2'$	457.56	15	218550	$^3P_2'-{}^3P_1$
1622.53	5	61632.2	$^3D_2-{}^3D_3'$	457.08	40	218780	$^3P_2'-{}^3P_2$
1611.27	0	62062.8	$^3D_2-{}^3F_2$	456.79	15	218918	$^3P_1'-{}^3P_1$
1607.04	0	62226.0	$^3D_3-{}^3F_3$	456.68	15	218971	$^3P_1'-{}^3P_0$
1603.17	60	62376.4	$^3D_1-{}^3F_2$	456.36	10?	219125	$^3P_0'-{}^3P_1$
1591.70	70	62825.9	$^3D_2-{}^3F_3$	456.31	20	219149	$^3P_1'-{}^3P_2$
1579.67	80	63304.3	$^3D_3-{}^3F_4$	446.71	5	223859	$a^1D_2-{}^1F_3$
1519.02	70	65831.9	$b^1D_2-{}^1F_3$	441.11	40	226701	$a^1D_2-{}^1P_1$
1498.02	70	66754.8	$^3D_3-{}^3P_2$	438.66	50?	227968	$a^3F_4'-{}^3D_3'$
1489.75	50	67125.3	$^3D_2-{}^3P_1$	438.65	40?	227972	$a^3F_3'-{}^3D_2'$
1484.67	15	67355.0	$^3D_2-{}^3P_2$	438.62	30?	227988	$a^3F_2'-{}^3D_1'$
1482.89	25	67435.9	$^3D_1-{}^3P_1$	437.69	20	228472	$a^3F_2'-{}^3D_1'$
1481.69	30	67490.5	$^3D_1-{}^3P_0$	437.43	20	228608	$a^3F_3'-{}^3D_3'$
1455.27	30	68715.7	$b^1D_2-{}^1P_1$	436.61	20	229037	$a^3F_3'-{}^3F_2$
1131.16	2	88404.8	$^3F_4-{}^3G_4$	436.37	25	229163	$a^3F_4'-{}^3F_3$
1123.62	10	88998.0	$^3F_4-{}^3G_5$	435.66	25	229537	$a^3F_2'-{}^3F_2$
1121.98	0	89128.0	$^3F_3-{}^3G_3$	435.16	30	229800	$a^3F_2'-{}^3F_3$
1117.55	8	89481.4	$^3F_3-{}^3G_4$	434.33	40	230239	$a^3F_4'-{}^3F_4$
1112.47	6	89890.0	$^3F_2-{}^3G_3$	434.22?	?	230298	$a^3F_2'-{}^3F_3$
				433.13	5	230878	$a^3F_3'-{}^3F_4$

the once more ionized atoms, Fig. 1, shows that the two are almost identical as far as the slopes and relative positions of the heavy diagonals are concerned. Here again two relations may be mentioned, first, the *increased binding of a 3d electron over a 4p and a 4s electron* and second, *the parallelism existing between the lines 3d4s, 3d4p, and 3d4d.*

The ^2D term *limits* of all the terms shown in Fig. 4 are the low ^2D terms of Fig. 1 from which it may be seen that the diagram of Fig. 4 could have been built down from those limits on the diagram of Fig. 1, and still have obtained the same type of diagram and the same relations cited above. The ionization potentials, that is the voltage necessary to remove one *3d* electron from the

normal state $^3F_2(3d)^2$ of V IV and Cr V, to the normal state $^2D_2$ of the once more ionized atoms are determined at about 48.3 volts and 72.8 volts respectively.

The modified Moseley type of diagram has been extended to the sequence of iso-electronic systems Sc I, Ti II, V III, Cr IV, etc. and it has been found to be very similar to Figs. 1 and 4.

CORNELL UNIVERSITY,
December 19, 1928.

ON THE SPARK SPECTRUM OF NICKEL (Ni II)

By R. J. Lang

Abstract

Twenty-six lines resulting from intercombinations between the lowest terms $d^9\ ^2D_{2,3}$ and eleven more terms of the d^8p configuration b^4S', b^4P, b^4D'; c^2S', c^2P, c^2D'; b^2P, b^2D', b^2F; c^2F; b^2G'; have been classified. These lines lie between 1537 and 1250A.

IN A previous report[1] the lowest term of the Ni II spectrum $d^9\ ^2D_{2,3}$ was given, the term values found being $D_2 = -6884$, $D_3 = -8391$. These values were based on thirteen observed combinations between this low doublet D term and some of the d^8p terms.

TABLE I. *Predicted and observed lines in the spectrum of Ni II.*

Combination	ν(predicted)	ν(observed)	λ(I.A. vac.)	*I*
$^2D_3-b^2G_4'$	79820	79817	1252.86	2
$^2D_3-c^2F_4$	75914	75908	1317.38	15
$^2D_3-c^2F_3$	75886			
$^2D_2-c^2F_2$	74379	74380	1344.45	00
$^2D_3-b^4S_2'$	74297	74302	1345.85	3
$^2D_3-c^2P_2$	72982	72982	1370.20	9
$^2D_2-b^4S_2'$	72790			
$^2D_2-c^2S_1'$	72773	72773	1374.14	3
$^2D_2-c^2P_1$	72393	72392	1381.36	4
$^2D_3-c^2D_3'$	72372			
$^2D_3-c^2D_3'$	71768	71769	1393.36	2
$^2D_2-c^2P_2$	71475	71477	1399.06	1
$^2D_2-c^2D_2'$	70865	70867	1411.10	3
$^2D_3-b^4D_4'$	70774	70775	1412.92	2
$^2D_3-b^4D_3'$	70704	70707	1414.29	4
$^2D_3-b^4D_3'$	70632	70627	1415.89	2
$^2D_2-c^2D_1'$	70261	70265	1423.19	1
$^2D_2-b^4D_1'$	69238	69235	1444.35	1
$^2D_2-b^4D_2'$	69196	69190	1445.29	1
$^2D_2-b^4D_3'$	69125	69126	1446.64	2
$^2D_3-b^2P_2$	68962			
$^2D_3-b^2D_3'$	68732	68730	1454.96	4
$^2D_3-b^2D_2'$	68151	68151	1467.34	1
$^2D_3-b^2F_4$	68128	68127	1467.85	3
$^2D_3-b^2F_3$	67691			
$^2D_2-b^2P_2$	67455			
$^2D_2-b^2D_3'$	67225			
$^2D_2-b^2P_1$	66771			
$^2D_2-b^2D_2'$	66644	66645	1500.49	1
$^2D_3-b^4P_2$	66576	66572	1502.14	0
$^2D_3-b^4P_3$	66568			
$^2D_2-b^2F_3$	66184	66187	1510.86	1
$^2D_2-b^4P_1$	65521	65521	1526.22	0
$^2D_2-b^4P_2$	65069	65072	1536.76	0
$^2D_2-b^4P_3$	65061	65053	1537.20	0

[1] Lang, Phys. Rev. **31**, 773 (1928).

A further investigation has now been made and it has been found possible to locate the lines due to the intercombination of this lowest term with eleven more of the d^8p terms namely b^4S', b^4P, b^4D'; c^2S', c^2P, c^2D'; b^2P, b^2D', b^2F; c^2F; b^2G'. These lines all lie between 1537 and 1250A. The source employed was the vacuum spark between metallic nickel electrodes when a variable inductance was used in series with the spark. This inductance was increased until the source was quite weak necessitating long exposures, some of which reached as much as seven hours. The electrodes were placed very near together; in fact as close as possible without actually touching.

The first column of Table I shows the intercombinations expected, each followed in the second column by the calculated wave-number of the predicted line. The remaining three columns of the table give the wave-number, wave-length, and intensity of the observed lines. All the empirical d^8p terms of Ni II have now been found to combine with this low D term.

The notation and term values of the d^8p terms used in this report were taken from the analysis of Ni II by Shenstone,[2] while the term values of the d^9D terms are those quoted at the beginning of this paper.

The author takes this opportunity to thank Professor Shenstone for suggesting a further search for these combinations. A grant from the Research Council of Canada is also acknowledged.

EDMONTON, ALBERTA, CANADA,
January 8, 1929.

Note added in proof, March 16th. While this paper was in press an article appeared by Menzies (Proc. Roy. Soc **122,** 134, 1929.) in which most of these combinations were recorded.

[2] Shenstone, Phys. Rev. **30,** 255 (1927).

VARIATION IN THE INTENSITIES OF MERCURY SPECTRUM LINES WITH PRESSURE OF THE VAPOR

By John G. Frayne* and Carol G. Montgomery

Abstract

The relative intensities of spectrum lines of Hg vapor in the d.c. arc and at a pressure of 10^{-3} mm in a high frequency electrodeless discharge have been measured for wave-lengths ranging from 7000 to 3000A. There is a decided increase in intensity, relative to the triplet line 5460, of the singlet members in the low pressure discharge, the sharp series showing the greatest increases. The relative intensity increases rapidly with ascending members of the series. Five new lines in the sharp singlet series were observed. Combination singlets appeared strong in the red in the low pressure discharge. The first members of the triplet series do not show much change but the higher members show an increasing intensity at low pressure. Combination lines also show decided increase in the low pressure discharge.

IN ORDER to investigate the behavior of the spectrum of mercury vapor under widely different conditions of pressure, the spectrum as produced in an ordinary d.c. arc has been compared with the spectrum in the vapor at a room temperature of 20°C. The pressure in the arc being in the neighborhood of one atmosphere and that in the vapor at 20°C being approximately 10^{-3} mm, these two conditions allow comparison of the spectra for a pressure ratio of approximately 10^6 to 1.

In order to secure a strong discharge in the vapor at 20°C or at lower temperatures that might be necessary to use in the research, it was decided to use an electrodeless discharge at frequencies of the order of 10^8 cycles per second. The success which Wood and Loomis[1] had already reported in obtaining strong discharges in tubes already evacuated to a high degree indicated that there should be no difficulty in securing a strong discharge in mercury vapor at pressures of 10^{-3} or 10^{-4} mm.

An ordinary horizontal quartz arc was used for the high pressure spectra. A Pyrex window was placed in front of the spectrograph slit in order to allow comparison with the spectrum from the high frequency discharge apparatus which was made entirely of Pyrex glass. The arc was operated on a current of 3 amperes and was allowed to run for half an hour before any photographs were taken of the spectra. The power for the high frequency discharge was obtained from two R.C.A. UX-852 tubes connected in "push-pull" manner. Oscillations of 3 meter wave-lengths were strongly produced in this type of circuit. A solenoid of copper wire was wound on the discharge tube and coupled to the helix of the oscillating circuit. When this solenoid had a natural period corresponding to the frequency of oscillation, strong dis-

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[1] Wood and Loomis, Nature **120**, 510 (1927).

charges were produced in the tube containing mercury vapor at room temperature. This discharge was viewed end-on through a plane glass window.

The arc spectrum was photographed for periods ranging from one second to 16 minutes while the spectrum of the high frequency discharge was taken for periods ranging from 5 seconds to 4 hours. The plates were developed together in a tank in which a developing solution was continuously stirred. The density of the lines of each spectrum was then measured on a microphotometer and the densities of a given line for different exposure-times were plotted against the logarithm of the time of exposure. Practically all these curves had a straight line characteristic for densities ranging from around 0.4 to 1.2. All the data used in calculating intensity values shown in the table were obtained for a line-density of one. If the plate were equally sensitive to all wave-lengths these lines would be parallel. However, in the panchromatic plates used in this work the curves in the yellow and red regions of the spectrum were very nearly parallel in their straight line sections, while the curves in the blue and violet regions exhibited similar parallelism but with different slope from those of the long wave-length lines. On account of the varying sensitivity of the plate the relative intensities of the lines in one exposure will not be the true values. However, the intensity of any line in the arc relative to the intensity of the same line in the low pressure discharge will be correct within the limits of experimental error.

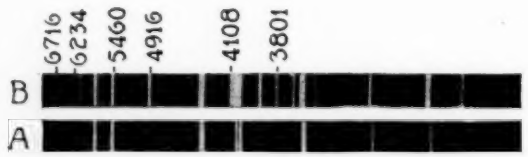

Fig. 1. Hg spectrum. *A*, d.c. arc; *B*, discharge at 10^3 mm.

The spectrum of Hg vapor under these two conditions is shown in photographs of Fig. 1. The red lines which occur so faintly in the arc are very prominent in the low pressure spectrum. The lines 4916 and 4108 appear very prominently at low pressure but are very faint in the arc. In addition to these very obvious changes in intensity of these lines one will observe many lines in the low pressure spectrum that do not appear at all in the arc or are so weak that they only appear very faintly in long exposures.

Referring to Table I it will be noticed that if we assign an arbitrary intensity of 100 to the line 5460 in each spectrum the intensity of the second member of this triplet series, 3341A, is increased nearly twentyfold in the low pressure discharge. The most marked increase of intensities is found in the sharp series of singlets, the intensity ratio for the line 4916 being 250 and increasing to 360 for the line 4108. These observations are in general qualitative agreement with the work of Hodges and Michels[2] of this laboratory who

[2] Hodges and Michels, Phys. Rev. **32**, 913 (1928).

report a similar increase in relative intensity of the singlets in the helium spectrum at low pressures.

In the diffuse series the first member, 5790A, is almost twice as strong at the low pressure as it is in the arc. It will be observed, however, that the

TABLE I. *Ratio of intensities of lines in the mercury spectrum in the d.c., arc and in the high frequency discharge at low pressure.*

Line	Designation	Low pressure discharge (10^{-3} mm)	d.c. Arc	Intensity Ratio
6716.45	7^1S-8^1P	2.8	—	∞
6234.35	7^1S-9^1P	18	—	∞
4916.04	6^1P-8^1S	50	0.2	250
4108.08	6^1P-9^1S	62	0.10	620
3801.67	6^1P-10^1S	14	0.01	1400
3558.60	6^1P-12^1S	1.2	—	∞
5790.66	6^1P-6^1D	50	26	1.9
3906.40	6^1P-8^1D	100	1.9	52
3704.22	6^1P-9^1D	20	.1	200
3592.97	6^1P-10^1D	0.5	—	∞
3524.27	6^1P-11^1D	1.5	—	∞
3478.98	6^1P-12^1D	0.7	—	∞
3447.22	6^1P-13^1D	0.1		
5460.74	$6^3P_2-7^3S$	100	100	1
3341.48	$6^3P_2-8^3S$	104	5.4	19.2
4358.34	$6^3P_2-7^3S$	3000	500	6.0
4347.50	$6^1P_1-7^1D$			
4046.56	$6^3P_0-7^3S$	750	405	1.8
3663.28	$6^3P_2-6^1D$			
3662.88	$6^3P_2-6^3D_{1,2,3}$	875	292	3.0
3654.83				
3650.15				
3131.84	$6^3P_1-6^1D$			
3131.56	$6^3P_1-6^3D_{1,2}$	925	5	185.0
3125.66				
6072.63	7^3S-8^1P	8	—	∞
5675.86	7^3S-9^1P	6.3	—	∞
4077.83	$6^3P_1-7^1S$	428	48	8.9
3027.48	$6^3P_2-7^1D$	13	—	∞
3025.62	$6^3P_2-7^3D_{1,2,3}$			
3023.47				
3021.50				
6123.		8	—	∞
4797.		1	—	∞
3984.		0.05	0.2	0.25

fourth member of this series, 3704A, is 200 times stronger at low pressure. The intensity ratio of the line 4347, the second member of the diffuse series, could not be measured as it could not be separated by the microphotometer from the triplet line 4358. The combination lines which could be resolved

showed increase in intensity in the low pressure discharge. However, the two strong combination lines 3663 and 3131 could not be resolved sufficiently as they have practically the same wave-lengths as two strong members of the diffuse triplet series. In addition to the increase in strength of the higher members of the singlet series several new members of the sharp singlet series, were observed. Five lines of shorter wave-length than the 3801 line, which is the last member of the series listed by Fowler[3] were observed on plates exposed to the low pressure discharge.

The authors wish to thank Professor I. S. Bowen, who initiated this line of investigation at this laboratory, for his constant interest in the work and his many helpful suggestions and criticisms. They also wish to thank Mr. W. C. Michels for his courtesy in setting his photographic development apparatus and microphotometer at their disposal.

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PASADENA, CALIFORNIA,
December 15, 1928.

[3] Fowler, "Report on Series in Line Spectra" (1922).

THE MOTION OF IONS IN CONSTANT FIELDS

By Leigh Page

Abstract

It is shown that the effect of a constant electrical or gravitational force $\boldsymbol{F}$ on ions passing through a constant magnetic field $\boldsymbol{H}$ is to cause the circular or helical ion paths to advance in a direction at right angles to both $\boldsymbol{F}$ and $\boldsymbol{H}$ with the constant velocity

$$\boldsymbol{u}=c[\boldsymbol{F}\times\boldsymbol{H}]/e\boldsymbol{H}^2.$$

Ion paths relative to a rotating earth are discussed on the assumption that the earth's field is purely magnetic relative to the inertial system of the center of the earth. The essential features of the theory are shown to be unaltered if the constant mass of the classical theory is replaced by the variable mass of the relativity theory.

IN DISCUSSING the motion of ions in a magnetic field it is often stated that the ions describe helices about the lines of force without consideration being given to the effect on the ion paths of other forces, such as those due to electrical or gravitational fields. The equations of motion of an ion in constant electric and magnetic fields have been given by many authors,[1] but usually in such a form that the nature of the path is not immediately evident. While the following discussion contains nothing essentially new beyond the method of treatment employed, the very simple description of the ion paths which is obtained may be of use, particularly to those who are interested in the effect of the earth's magnetic field on ions in the upper atmosphere.

We shall utilize the classical dynamics in our main discussion, showing later that the essential features of the theory are unaltered if the constant mass of the classical theory is replaced by the variable mass of the relativity theory.

Classical Dynamics

The equation of motion of an ion of mass m and charge e subject to a constant electrical or gravitational force $\boldsymbol{F}$ and a constant magnetic field $\boldsymbol{H}$ is, in Heaviside-Lorentz units,

$$m\boldsymbol{dv}/dt=\boldsymbol{F}+e[\boldsymbol{v}\times\boldsymbol{H}]/c \tag{1}$$

relative to the inertial system $x\ y\ z$ in which $\boldsymbol{F}$ and $\boldsymbol{H}$ are measured. The magnetic field has no effect on the component of the motion along the lines of force, the ion being subject only to a uniform acceleration equal to the component of $\boldsymbol{F}$ along the lines of force divided by m in so far as the motion in that direction is concerned. Therefore it is only the motion at right angles to $\boldsymbol{H}$ which requires discussion, and the generality of our results will be in

[1] J. J. Thomson, Cond. of Elect. through Gases, p. 112, Eq. (7), (8). (Thomson seems to use left-handed axes); L. Page, Phys. Rev. **24**, 284, Eq. (1), (2), (3).

no way impaired by assuming *ab initio* that both $\boldsymbol{v}$ and $\boldsymbol{F}$ are perpendicular to $\boldsymbol{H}$ and therefore that the motion is confined to a plane. For the sake of definiteness we shall suppose $\boldsymbol{H}$ to be along the z axis, $\boldsymbol{v}$ and $\boldsymbol{F}$ lying in the x y plane.

Now consider a set of axes X Y Z parallel respectively to x y z and moving relative to the latter with the constant velocity

$$\boldsymbol{u}=c[\boldsymbol{F}\times\boldsymbol{H}]/e\boldsymbol{H}^2. \tag{2}$$

If we denote the velocity of the ion relative to X Y Z by $\boldsymbol{V}$ then

$$\boldsymbol{V}=\boldsymbol{v}-\boldsymbol{u}, \quad d\boldsymbol{V}/dt=d\boldsymbol{v}/dt, \tag{3}$$

and the equation of motion (1) becomes

$$m d\boldsymbol{V}/dt=e[\boldsymbol{V}\times\boldsymbol{H}]/c \tag{4}$$

when referred to the new axes. By referring the motion to these axes we have eliminated the field $\boldsymbol{F}$. The motion described by (4) is motion with constant speed V in a circle of radius

$$\rho=mcV/eH \tag{5}$$

in the clockwise sense for positive e, the angular velocity being

$$\boldsymbol{\omega}=-e\boldsymbol{H}/mc, \tag{6}$$

which, incidentally, is just twice the Larmor precession obtained by neglecting the centrifugal reaction and taking into account only the Coriolis reaction.

The integrated equations of motion relative to the moving axes are obviously

$$\begin{aligned} X&=X_0+\frac{mc}{eH}\,V\cos\frac{eH}{mc}(t+\delta), \\ Y&=Y_0-\frac{mc}{eH}\,V\sin\frac{eH}{mc}(t+\delta), \end{aligned} \tag{7}$$

X_0, Y_0, being the coordinates of the center of the circular orbit. We note that these equations contain four arbitrary constants X_0, Y_0, V, δ, and therefore they constitute the complete solution of the differential equations of motion. If we refer the motion to the axes x y z we are led at once to the equations referred to in footnote 1.

The simple analysis developed above shows that the effect of a constant electrical or gravitational force $\boldsymbol{F}$ *in an inertial system* x y z *is*: (1) *to change the radius of the circular path of an ion about the lines of magnetic force from*

$$\frac{mc}{eH}v_0 \quad \text{to} \quad \frac{mc}{eH}(v_0^2-2\boldsymbol{u}\cdot\boldsymbol{v}_0+u^2)^{1/2} \tag{8}$$

where v_0 represents the initial velocity of the ion relative to x y z; and (2) *to cause the circular path to advance relative to x y z with the constant velocity* $\boldsymbol{u}$ *given by* (2) *in a direction at right angles to both* $\boldsymbol{F}$ *and* $\boldsymbol{H}$. In this latter respect the effect of the force $\boldsymbol{F}$ is analogous to that of a force applied to a gyrostat in that it gives rise to a motion at right angles to itself.

The path of an ion relative to x y z is therefore a cycloid. According as V is greater than, equal to, or less than u, the cycloid is curtate, common, or prolate. If we denote the initial velocity of the ion relative to x y z by $\mathbf{v}_0$ and the angle between $\boldsymbol{u}$ and $\boldsymbol{v}_0$ by θ then we have from (3)

$$V^2 = v_0^2 - 2uv_0 \cos\theta + u^2. \tag{9}$$

For a common cycloid $V = u$ and either $v_0 = 0$ or

$$\cos\theta = v_0/2u. \tag{10}$$

We can classify all possible cases as follows:

(1) $V = 0$. This case exists only when $v_0 = u$ and $\theta = 0$. The path is a straight line at right angles to $\boldsymbol{F}$ and $\boldsymbol{H}$, the force due to the magnetic field being just balanced by $\boldsymbol{F}$.

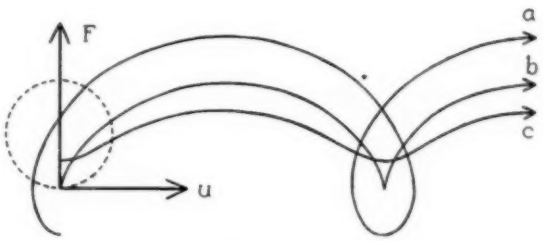

Fig. 1.

(2) $V \neq 0$. We have three subcases, namely:

(a) $v_0 = 0$. The path is a common cycloid, the ion starting at the cusp.

(b) $0 < v_0 \leqq 2u$. The path is a prolate cycloid, common cycloid or curtate cycloid according as the angle θ is less than, equal to, or greater than that defined by equation (10).

(c) $2u < v_0$. The path is a curtate cycloid for all values of θ.

These three types of path are illustrated in Fig. 1 for positive e, the magnetic field being perpendicular to the paper and directed toward the reader. The radius of the rolling circle

$$r = mcu/eH \tag{11}$$

is independent of the initial velocity v_0. It is determined solely by the fields $\boldsymbol{F}$ and $\boldsymbol{H}$ and by the charge and mass of the ion. The distance of the generating point from the center of the rolling circle, given by (5), depends in addition upon the magnitude and direction of the initial velocity v_0, as is shown by (9). Curve a represents a curtate cycloid, b a common cycloid and c a prolate cycloid, all for the same value of u. The common rolling

circle is indicated by a broken line. As is clear from the fact that u is not a function of v_0 the drift velocity of progression perpendicular to $\boldsymbol{F}$ and $\boldsymbol{H}$ is independent of the initial velocities of the ions or the particular type of cycloid described.

If the non-magnetic force is due to an electric field, $\boldsymbol{F}=e\boldsymbol{E}$, and the charge disappears from the equation (2) for the velocity of progression. Therefore positive and negative ions drift in the same direction and with the same speed in an electric field whatever their masses or the magnitudes of their charges may be. The paths of the negative ions are obtained from those of the positive ions depicted in the figure by rotating the diagram through 180° about a horizontal axis.

On the other hand, if the non-magnetic force is due to a gravitational field, $\boldsymbol{F}=m\boldsymbol{g}$ and (2) becomes

$$u=cmg/eH$$

In this case ions of opposite sign drift in opposite directions with speeds inversely proportional to the ratio of e to m. Thus a current is produced, which, in the case of the earth, is from west to east and therefore in such a direction as to tend to demagnetize the earth.

In order to obtain an estimate of the magnitude of the drift which would exist if no collisions took place, let us consider an ion of atomic mass A projected across the lines of force of the earth's magnetic field at the equator and subject to the earth's electric and gravitational fields. For the purpose of calculation assume

$H=0.5$ gauss $=0.14$ H. L. U. (Heaviside-Lorentz Units)
$E=100$ volts/meter $=0.94\ (10)^{-3}$ H. L. U.
$e=4.77\ (10)^{-10}$ E. S. U. $=1.69\ (10)^{-9}$ H. L. U.
$m=1.65\ (10)^{-24}\ A$ gm

The drift velocity due to the earth's electric field is then

$$u_e=cE/H=2(10)^8 \text{ cm/sec}$$

and that due to the earth's gravitation field is

$$u_g=c\frac{mg}{eH}=0.2A \text{ cm/sec}.$$

For ions projected into the earth's magnetic field near the surface of the earth with velocities of the order of magnitude of $(10)^8$ cm/sec the drift due to gravity is negligible, although that due to the earth's electric field is of the same order of magnitude as the velocity of projection.

Finally we shall consider the relation between the ion paths relative to an inertial system S with origin at the center of the earth and those relative to the inertial system S' of an observer stationed on the earth at the equator. On account of the rotation of the earth S' has an eastward velocity relative to S of $4.7\ (10)^4$ cm/sec.

We shall neglect the small drift due to the earth's gravitational field and furthermore we shall suppose that relative to S the earth's field is purely magnetic, no accompanying electric field being present. Then the ions, if projected with velocities of $(10)^8$ cm/sec relative to S, will describe stationary circles relative to this inertial system of a radius of 200 A meters according to equation (5). Therefore the ion paths will progress to the west with a drift velocity of 4.7 $(10)^4$ cm/sec relative to the observer stationed on the earth at the equator.

How is the observer in S' to account for this progression? The transformations for the electromagnetic field give the answer at once. If v designates the eastward velocity of 4.7 $(10)^4$ cm/sec of S' relative to S, the observer in S' is aware[2] of the electric field (induced electromotive force)

$$\boldsymbol{E}' = k[v \times \boldsymbol{H}]/c$$

in addition to the magnetic field $\boldsymbol{H}' = k\boldsymbol{H}$, where

$$k \equiv (1 - v^2/c^2)^{-1/2}$$

This electric field gives rise to a drift

$$\boldsymbol{u}' = c[e\boldsymbol{E}' \times \boldsymbol{H}']/eH'^2 = -v$$

according to (2). Therefore the analysis of the problem from the point of view of the observer stationed on the earth agrees with that of the observer in the inertial system S.

Relativity Dynamics

If we make use of the variable mass of the relativity theory in place of the constant mass of the classical theory the essential features of the preceding theory remain unchanged. Suppose that we have mutually perpendicular constant fields $\boldsymbol{E}$ and $\boldsymbol{H}$ relative to an inertial system S. We shall orient our axes so that the Y axis is parallel to $\boldsymbol{E}$ and the Z axis to $\boldsymbol{H}$.

Now consider a second initial system S' which has a velocity $\boldsymbol{u}$ along the X axis equal to

$$\boldsymbol{u} = c[\boldsymbol{E} \times \boldsymbol{H}]/H^2 \tag{12}$$

The transformations[2] for $\boldsymbol{E}$ and $\boldsymbol{H}$ give us for the electric field $\boldsymbol{E}'$ and magnetic field $\boldsymbol{H}'$ in S'

$$\begin{aligned} \boldsymbol{E}' &= k\left\{\boldsymbol{E} + \frac{1}{c}\boldsymbol{u} \times \boldsymbol{H}\right\} = 0, \\ \boldsymbol{H}' &= k\left\{\boldsymbol{H} - \frac{1}{c}\boldsymbol{u} \times \boldsymbol{E}\right\} = k\boldsymbol{H}\left(1 - \frac{E^2}{H^2}\right), \end{aligned} \tag{13}$$

where $k \equiv (1 - u^2/c^2)^{-1/2}$.

[2] L. Page, Introduction to Electrodynamics p. 24.

As in the previous treatment we have eliminated the electric field by passing over to the inertial system S'. The equation of motion relative to S' is

$$\frac{d}{dt'}\left\{\frac{m\boldsymbol{V}'}{(1-V'^2/c^2)^{1/2}}\right\}=\frac{e}{c}\boldsymbol{V}'\times\boldsymbol{H}', \tag{14}$$

where $\boldsymbol{V}'$ is the velocity of the ion relative to this system. This is the equation of motion in a circle with constant speed V', the radius of the circle and the angular velocity being given by (5) and (6) respectively provided we replace $\boldsymbol{V}$ by our present $\boldsymbol{V}'$ and put the transverse mass

$$m(1-V'^2/c^2)^{-1/2}$$

of the relativity theory in place of the constant mass m of the classical theory.

Therefore the relativistic treatment of the problem leads to essentially the same results as that based on the classical dynamics, although it emphasizes the fact that we must confine our conclusions to cases where E is less than H so that u may be less than c.

Note. Dr. Hulburt has kindly drawn the author's attention to the fact that some of the conclusions of this paper have already been recognized by others. In the paper of Ross Gunn[3] the average drift velocity of an ion in the direction at right angles to applied electric and magnetic fields has been calculated and shown to be independent of the initial velocity. The nature of the ion paths, however, has not been investigated.

In Nature, Chapman[4] refers to the "drift acquired by charges under the joint action of the magnetic field, gravity and the vertical electrostatic field" of the earth, and makes the statement that "the drift is westward for the electrons and eastward for positive ions." This statement, while true for the gravitational drift, is not correct for the electrical drift.

Finally Maris and Hulburt[5] state that "ions, no matter what their velocities are, under the combined action of gravity and the earth's magnetic field, move at right angles to these two vectors with a velocity approximately mg/He, the positive and negative ions moving in opposite directions."

Sloane Physics Laboratory,
Yale University,
January 10, 1929.

[3] Gunn, Phys. Rev. **32,** 135 (1928).
[4] Chapman, Nature **122,** 572 (1928).
[5] Maris and Hulburt, Nature **122,** 807 (1928).

ANGULAR SCATTERING OF ELECTRONS IN HELIUM, NEON, HYDROGEN AND NITROGEN

By G. P. Harnwell*

Abstract

An attempt has been made to investigate in a qualitative way the angular distribution of electrons scattered by a gas. The gases which were used were helium, neon, hydrogen and nitrogen. The energy of the primary beam of electrons varied from 75 to 300 equivalent volts. It was found that those electrons which were scattered elastically were deflected in general through only a few degrees. In helium less than one-thousandth of the 200 volt electrons were scattered through 15°. Electrons which had sustained an exciting collision were scattered through slightly larger angles. Evidence of electrons which had suffered two inelastic collisions was obtained, these were distributed through still larger angles. A general tendency for slower electrons to be scattered through larger angles was observable.

THE problem of the angular scattering of electrons in gases is one which has been attacked by indirect methods by several investigators. In particular, Langmuir[1] has obtained very interesting evidence on the angular distribution of electrons scattered by mercury vapor in a discharge tube. The method used was an indirect one but very definite conclusions as to the variation of angular scattering with the energy were reached. These results are capable of verification by a more direct means.

During the progress of the present work two further papers have appeared bearing on the extremes of angular scattering. A paper by Jones and Whiddington[2] dealt with their investigation of 0° scattering in hydrogen. They found that of those electrons which were undeflected from their original beam by far the largest proportion had lost no energy at all. There were a few electrons which had lost amounts of energy varying from 0 to 12.26 volts. A large number of electrons were observed which had lost 12.26 volts, there was also a small number of electrons which had lost more than this amount, and some evidence pointed to a small group of electrons which had lost 24.5 volts. The energy of the electrons was determined by analysis in a magnetic field.

The second paper is by R. Kollath.[3] He investigated the electrons scattered through 90° in various gases. He used only slow electrons and found that of the order of one percent of the electrons were scattered through this large ang'e. The scattered electrons were practically homogeneous and had lost no energy; this was determined by applying a retarding potential to the collector. Scattering at right angles was found to depend very markedly

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[1] Langmuir, Phys. Rev. **31**, 357 (1928).

[2] Jones and Whiddington, Phil. Mag. **6**, 889 (1928).

[3] Kollath, Ann. d. Physik **87**, 259 (1928).

on the primary energy of the electrons and the ionization potential of the gas which was employed in the scattering.

The present investigation has been concerned with the angular scattering of electrons in the four gases, helium, neon, hydrogen, and nitrogen. Angles varying from 0° to 90° were used. The energy of the primary electrons was in the range from 75 to 360 equivalent volts. The energy of the scattered electrons was measured by an electrostatic filter.

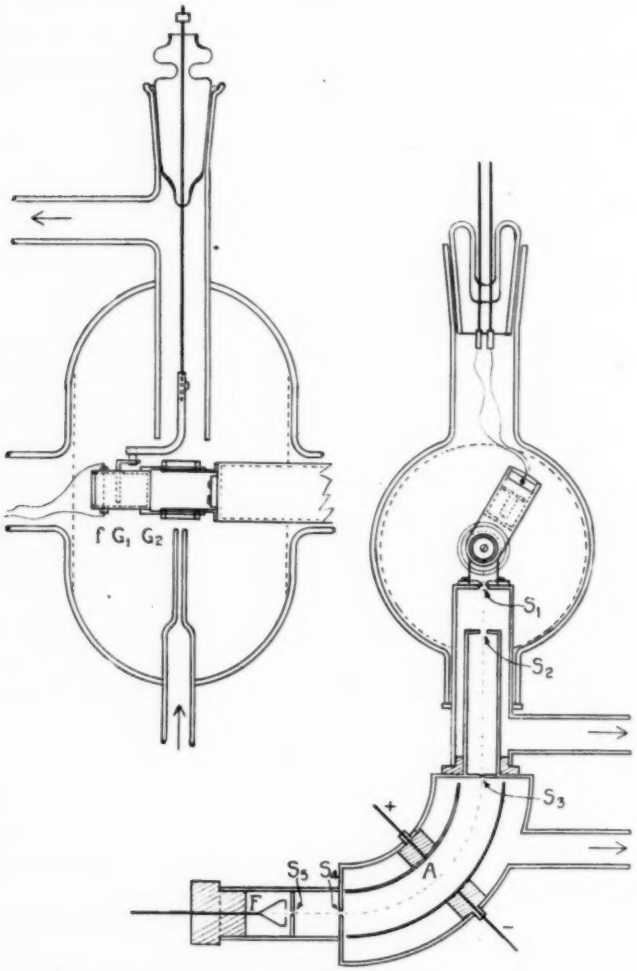

Fig. 1. Diagram of apparatus.

The apparatus used was in a general way similar to that used by Dymond[4] and by the present writer.[5] The main points of difference were in the mounting of the electron gun, in the arrangements for admitting the gas, and in the analysis of the scattered electrons. The apparatus is represented diagrammatically in Fig. 1.

[4] Dymond, Phys. Rev. **29**, 433 (1926).
[5] Harnwell, Proceedings of the Nat'l. Academy **14**, 564 (1928).

The electrons were supplied by a 4 mil thoriated tungsten filament. This was formed in the shape of a very narrow hairpin to reduce the magnetic effect of the filament current. It was mounted in the rear of the short thick-walled copper tube which formed the electron gun. The filament current was supplied through rather long flexible leads to allow for the motion of the electron gun. Immediately in front of the filament was a large slit or diaphragm which will be referred to as D. This was insulated from the filament and from the rest of the tube forming the gun. A constant potential was in general maintained between the filament and this diaphragm to supply the electron stream. A second slit about half a millimeter wide formed the front of the electron gun. This determined the width and direction of the electron beam and also by varying the potential difference between it and the filament it determined the energy of the electrons emerging from the gun. The entire gun was made of copper, the necessary insulation was obtained by means of mica sheet which gave some trouble till by repeated heating it had become, as nearly as possible, outgassed.

Two arms extended about a centimeter and a quarter forward from the top and bottom edges of the gun. At the ends of these arms were holes about a centimeter in diameter. Two similar arms extended out from the face of the analyser. In the end of each of these was a short section of thin walled brass tubing, about one centimeter outside diameter, and a millimeter long. These arms sprang apart slightly so that when the holes in the arms of the gun were placed over the short lengths of tubing the gun was held in position. It was able to rotate through about 100° on both sides of the zero position about the center of the holes as an axis. The front slit of the gun was about 0.75 cm from this axis.

The face of the analyser which supported the gun also contained an adjustable slit. This was about a centimeter and a half from the axis about which the gun revolved. It was made as fine as possible, about a tenth of a millimeter throughout the following work. It served to determine the beam of scattered electrons entering the analyser and also to maintain as great a difference of pressure as possible between the scattering chamber and the analyser. The inside of the scattering chamber was lined with copper gauze for purposes of electrostatic shielding. The body of the gun, including the front slit, the part of the analyser projecting into the scattering chamber, and the copper gauze were all maintained at the same potential, so that as nearly as possible the scattering chamber was free of any electric fields.

The region immediately behind the first slit S_1 of the analyser was evacuated by a mercury diffusion pump through a liquid air trap. About a centimeter behind this slit was another slit S_2 about a millimeter wide, which was insulated from S_1 but metallically connected with the main body of the analyser. The purpose of this arrangement was to enable a field to be applied between S_1 and S_2 to accelerate electrons which entered the analyser. This was only resorted to when working with electrons whose original energy was less than 75 volts. Above 75 volts, S_1 and S_2 were generally kept at the same potential. Below 50 volts the action of the analyser was not satisfactory. The small residual magnetic field distorted its normal characteristics.

Slits S_3 and S_4 were about two millimeters in width. Between them the electrons were deflected through 90° by the difference in potential between the two curved plates, insulated from the body of the analyser, in chamber A. The action of this analyser is very simple but its disadvantage is that it does not differentiate between velocities but only between energies. However, if only electrons are used the masses are all equal and the energy determines the velocity. Additional resolution was obtained by a fifth slit S_5, one millimeter in width situated immediately in front of the Faraday cylinder. This latter was supported in an ebonite plug. As can be seen by reference to Fig. 1, there was an additional pumping exit from chamber A.

The gas employed for the scattering was admitted through a capillary tube of approximately two millimeters bore. This tube was arranged along the axis about which the gun revolved and the open end extended up to within a few millimeters of the lower of the two arms supporting the gun. Coaxially with this tube and a few millimeters above the upper arm was a large bore glass tube through which a high speed mercury diffusion pump exhausted the region immediately above that in which the scattering took place. It was found that by this arrangement a higher concentration of gas could be maintained in the scattering region than by any other method that was tried. The limiting condition, of course, is the low pressure which must be maintained in the analyser. An endeavor was also made to avoid an arc in the scattering chamber as it was feared that under those conditions disturbing effects would be introduced. In the following work where curves were obtained in the presence of an arc this will be mentioned specifically. It only occurred when working with electrons of low primary energy. It should be mentioned that the ends of the two glass tubes extending into the scattering chamber were covered with metal caps which were connected with the copper screen and other metal in the chamber to ensure as nearly as possible the absence of an electric field.

Down through the center of the exhausting tube extended a tungsten and copper rod in the end of which was a key which fitted snugly into a slit in the electron gun. This supplied a metallic connection with the first diaphragm D of the gun and also a method of rotating the gun under vacuum. This tungsten rod was supported in a ground glass stopper as shown on the diagram. Angles were read either by a beam of light reflected from a small mirror carried by the stopper or by a pointer arm and protractor. Because of the torsion play in the rod, angles could not be measured with an accuracy of greater than one degree.

The scattering chamber and analyser were placed at the center of a cubical frame of wire coils sixty centimeters on a side for neutralizing the earth's and any other stray magnetic fields. The coils were found necessary for electrons of even as high as 200 volts energy as the total path of the electrons was about 18 centimeters, and the maximum allowable deflection less than a millimeter. It was found that the magnetic effect of the filament current had also to be taken into consideration. However, this could only be partially compensated by the external coils. This introduced a certain

amount of difficulty as the magnetic field had to be adjusted empirically for different values of the current. The method of adjusting the compensating magnetic field was as follows. With no gas in the apparatus the gun was set at its zero position so that the primary beam was directed straight into the analyser. The potential across the plates in the analyser was set at its proper value and the magnetic field was varied till a maximum number of electrons reached the collecting electrode.

Considering only those electrons moving in a circle between the plates the following relation is easily obtained. Let V_1 equal energy of electrons, V_2 equal the potential between the plates, and d equal the distance between the plates, then the electric force toward the center of rotation is: $F_e = V_2 e/d$. The centrifugal force is: $F_m = mv^2/r$ or as: $mv^2/2 = V_1 e$, $F_m = 2V_1 e/r$. These are equal so:

$$V_1 = rV_2/2d.$$

This gives the relation by which the energy of the electrons may be calculated from the analyser potential. This relation was found to be strictly fulfilled except for very small values of V_1, where various disturbing effects appeared.

A final point which should be mentioned is that of the variation with angle of the actual volume of gas concerned in the scattering. Theoretically the volume concerned is that common to the two dihedral angles formed by the filament and slit of the gun, and collector and slit of the analyser. These angles are small and to a sufficient degree of approximation the sides may be taken as parallel. For this limiting condition the volume, except in the case of very small angles, would be inversely proportional to the sine of the angle. There are, however two further considerations. The first is that the contribution from each small element of this volume is not equal. Because of the high gas density a fraction of the electrons scattered from the regions farthest from the analyser will be again scattered and fail to reach the collector. Conversely, those electrons scattered near the collector slit will have a better chance of being recorded than those from the central part of the volume effective in the scattering. The accuracy of the results is not sufficient to justify a detailed examination of this question. The second consideration in a measure offsets this effect. Because of the method of admitting the gas it is probable that a cross section of the region of greatest density is not greater than a few square millimeters. Almost all of the electrons are scattered from this region. This is the justification for neglecting the first of these two considerations. It also greatly reduces the variations of the scattering volume with angle. As the exact weights of these various factors can not be measured in the present apparatus, the curves which will be given later are uncorrected for the angular variations of the volume concerned in the scattering.

The two rare gases which were used were helium and neon. These were obtained in a fairly pure state and further purified in the containers, from which they were drawn directly into the apparatus, by means of a Misch metal arc. The hydrogen which was used was prepared electrolytically and

dried by passage over phosphorus pentoxide and through a liquid air trap. The nitrogen was generated from ammonium nitrite and dried in the same way. The gases entered the apparatus through artificial leaks. The pressure in the scattering volume was varied by varying the pressure behind the leaks. A McLeod gauge was connected as closely as possible to the tube entering the scattering chamber. However, due to the distance involved and the diameter of the tubing admitting the gases to the scattering chamber, it is probable that the actual density of the gas in the scattering region was that corresponding to a pressure about half that recorded by the McLeod gauge. Gas pressures of the order of 0.1–0.3 millimeters were generally used as it was found that these were the greatest pressures at which the apparatus gave satisfactory results.

Helium.—The first case which will be discussed is the scattering in helium of electrons with energy equal to 75 equivalent volts. As has been previously

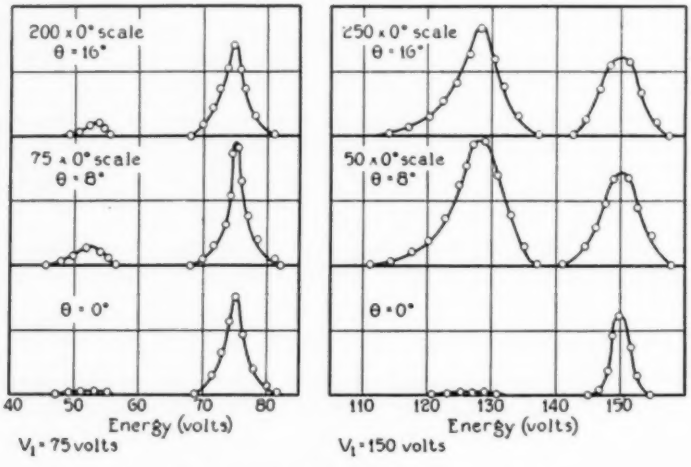

Fig. 2. Typical scattering curves for He.

mentioned the angle between the incident and scattered beam is the measurement most subject to error. In the following discussion when two curves are given as having been obtained at the same angle it is to be remembered that the exact value of the angle is only known with an accuracy of plus or minus 1 degree. It should also be mentioned that this analyser has a characteristic in common with the magnetic analyser in that the shape of the curves, though always symmetrical, is not independent of the energy of the electrons. The peaks are very narrow when electrons have a small energy, but as the energy of the primary beam increases, the peaks become quite broad.

A typical series of curves obtained in helium is given in Fig. 2. In these curves the electrometer current which represents the number of electrons entering the collecting electrode, is plotted against the energy of the electrons. These curves were obtained at a pressure as registered by the McLeod gauge of 0.2 and 0.3 millimeters. It may be estimated that the electrons on the average suffer one or two collisions in passing through the region of high

pressure. When no gas is present in the apparatus the peak at 0°, which is the only one observable, is perfectly symmetrical. But when helium is admitted it can be seen that the curves slope less sharply on the low voltage side. In the case of helium this effect is as great in the case of the primary peak (due to elastic collisions) as in the case of the secondary peak (due to partially inelastic collisions). The exact value of this slope seems to be a function of the angle though it only varies between narrow limits. This has not been investigated extensively, but for many combinations of angle and voltage in helium the primary peak slopes more gradually on the low voltage side than does the secondary peak. This is not true in the diatomic gases which will be mentioned later. The reason for this is not clear but it is probably connected with the fact that the secondary peak is associated with a radiating potential as will be discussed later. This asymmetry of the peak decreases with the gas pressure and undoubtedly represents the presence of electrons which have lost a small amount of energy of the order of one to four volts by some presumably elastic process. However, the maximum energy which could classically be lost in an elastic impact is of the order of 1/1000 of the original energy, and in that case there would be no forward component of the velocity. As some of these electrons have lost nearly 5 percent of their energy and still continue in their original direction, or are deflected less than one degree, the result is certainly inexplicable classically.

At angles greater than 0° it will be seen that there is a large number of electrons which have lost a definite amount of energy. The mean value of the energy loss from a large number of observations is 22 volts. This definitely identifies the energy loss as due to the numerous excitation potentials of helium in this region, rather than to the ionizing potential.

Confirmatory evidence is given by the shape of this secondary peak. For if this represents those electrons which had ionized a helium atom it might be expected that the secondary peak would be very much broader on the low voltage side than the primary peak, for energy in excess of the ionizing energy could be carried off in continuous amounts by the liberated electrons. Reference to Fig. 2 will show that this is not so. These peaks are of much the same shape as the primary peaks. Also it might be expected if ionization occurred, that a broad peak would appear at voltages from zero to $V_1 - 24.5$ volts representing those electrons ejected from the helium atoms. No such peak was observed, however, this is not conclusive as the intensity might well have been below the sensitivity of the electrometer, owing to the fact that this group of electrons is distributed over such a wide range of energies. Except at 0° the variation, if any, with pressure of the ratio of the primary to the secondary peak is very slight. Of course, at 0° as the pressure decreases the primary peak increases as there are fewer collisions, and the secondary peak decreases for the same reason. This is only so when the original beam of electrons is directed straight into the analyser. When only scattered electrons enter the analyser the peak ratio remains approximately constant. This is to be expected for there is no reason, except for multiple scattering, to suppose that the ratio of elastic to inelastic collisions is a

function of the pressure. Evidently the effects observed are due to single scattering.

As can be seen from Fig. 2 the number of electrons scattered at these high voltages decreases very rapidly as the angle between the primary beam and the scattered beam increases. In the case of 75 volt electrons some are scattered through angles as great as 25° or 30° but in general the scattered electrons are confined to a region much more closely surrounding the original beam. The amount of scattering at any angle is certainly a function of the primary voltage.

The general tendency is that the slow electrons are scattered most. The following table gives very approximately the angle at which the number of elastically scattered electrons in helium is reduced to 1/1000 of its value at 0°.

$V_1 =$	75	150	200
$\theta =$	22°	18°	15°

This table is of interest but the values of the angle θ can not be taken as having any particular significance. They would be different for a different value of the pressure on account of the electrons at 0° which enter the analyser without colliding, as can be seen from the preceding paragraph, and the pressure could not be kept accurately constant. However, they may be relied on to give the general tendency of the scattering. Kollath[3] found very appreciable numbers of electrons scattered through 90° in the neighborhood of the critical potentials, and preliminary experiments by the present writer which will be reported later, show the same results.

The ratio of the intensity of the secondary peak to the intensity of the primary peak also shows some very interesting variations with angle and voltage. At 0° for all voltages this ratio is seen to be very small. The secondary peak at that angle is barely distinguishable. At first sight this might be thought to be due to the large number of electrons entering the analyser which have come through the high pressure region without colliding. However, this is inadmissible as a complete explanation for two reasons. The first is that when the thermionic current is kept constant, at the pressure used the 0° peak was less than one-tenth its value when no gas was present. Thus at least nine-tenths of the electrons suffered collisions sufficient to deflect them from the original beam. Under these circumstances from the data given by Compton and Van Voorhis[6] approximately one ionizing collision is made per centimeter. The mean free path between exciting collisions is presumably still smaller. Hence a very large percentage of the original beam should have made exciting collisions, and if the electrons had a large probability of continuing in the forward direction a secondary peak quite comparable in magnitude with the primary peak should occur. The second reason for not considering the smallness of the secondary peak to be due to a lack of exciting collisions is that in the case of hydrogen, which will be discussed later, the secondary peak at 0° is quite comparable to the primary peak. If the probability of an exciting collision is of the same order of magnitude as the probability of an ionizing collision, the difference between the two gases

[6] Compton and Van Voorhis, Phys. Rev. **27**, 724 (1926).

can not be attributed to a very great difference between the probabilities of an exciting collision in these gases. For from the data of Compton and Van Voorhis only about twice as many ionizing collisions are made per centimeter in hydrogen as in helium, whereas the ratio of the secondary peak to the primary peak at 0° in hydrogen is twenty to thirty times what it is in helium. The only explanation, therefore, of the smallness of the secondary peak at 0° is that an electron which suffers an exciting or ionizing collision in helium has only a very small chance of proceeding on in its original path. There is very little variation of the size of this secondary peak or in the ratio of it to the primary peak with voltage. There is some evidence that at voltages above 300 it increases appreciably, but this is doubtful. Judging from the ionization free path there is probably little change in the mean free path between exciting collisions in this voltage region. The probability of ionization varies only very slightly though this might account for the possible increase of the secondary peak at voltages in the neighborhood of 300.

On examining the electrons which are scattered at a small angle, for instance, 8° as given in Fig. 2 a very marked change in the ratio of the peaks appears. The absolute areas of all the peaks decrease, though not so markedly as it would seem from Fig. 2, for it can be seen that they must be multiplied by a factor depending on the sine of the angle since the scattering is presumably symmetrical around the cone of angle θ about the original beam. But the ratio of the secondary peak to the primary peak increases several fold even at the lowest voltage. At this angle the ratio also increases with the voltage up to about 150 volts from which value it appears to decrease slightly. It attains about the same size as the primary peak between 100 and 150 volts. At 16° and 75 volts the ratio does not change greatly from what it was at 8° but from that point the variation with voltage is very rapid and the peaks are equal somewhere between 75 and 100 volts. From there on up to 350 volts the secondary peak continues to be larger. At 24° and 75 volts, the secondary peak is larger than the primary one and the scattering at this angle at higher voltage is too weak to be detected.

Because of the slight change particularly in magnetic field inherent in the motion of the electron gun, the numerical values of the areas of the peaks are not accurately comparable, but the values obtained can certainly be relied on in a qualitative way. The general picture of the scattering as given by these curves is then the following. The number of electrons scattered elastically decreases very rapidly as the angle between their path and the original beam increases. The effect of increasing the voltage is to concentrate these electrons more within those solid angles close to the original beam. The fraction of the electrons which are scattered inelastically is a function of the voltage, presumably approximately that given by the work of Compton and Van Voorhis. These electrons have not the same tendency to be confined to those angles close to the original beam. As the angle increases beyond a certain minimum angle, which may be 0° the concentration of these electrons diminishes, but not as rapidly as for the elastically scattered electrons. Throughout the range investigated for electrons with an energy of 100 volts or more an angle could always be found beyond which there were more electrons scattered in-

elastically than elastically. On going to higher voltages this angle decreased. At higher voltages these inelastically scattered electrons also tended to become more concentrated in those solid angles close to the original beam. The evidence is not sufficiently accurate to say definitely whether the tendency of the inelastically scattered electrons to concentrate about the axis with increasing voltage is strictly proportional to the same tendency seen in the elastically scattered electrons, or whether these two processes may occur at different rates.

Before leaving the subject of helium it should be mentioned that in the curves obtained at voltages above 300 volts there was evidence of electrons which had lost twice the radiating energy. The intensity of the peaks due to these electrons was not sufficiently great to enable them to be studied. At 360 volts this peak appeared to decrease less rapidly as the angle increased than did the other peaks. This is in general what would be expected if this peak were due to electrons which had suffered two collisions for the angular variation would be almost obliterated.

Neon.—The behavior of the electrons scattered in neon was in many respects similar to that observed in helium. The mean distance between the peaks was in this case 18 volts instead of 22. This also fits in very well with the conclusion that this energy loss represents a radiating potential, or the mean of several radiating potentials. At 0° the secondary peak is practically absent below 200 volts, above that potential it increases slightly but is never large; this might be interpreted as showing that neon tends to scatter these electrons which have collided inelastically through large angles. This conclusion is supported by other evidence. It should be mentioned that it is more difficult to interpret the curves obtained in neon because the peaks are closer together, and at high electron velocities the curves do not drop to the axis between peaks.

In general it may be said that electrons which have suffered elastic collisions are deflected through larger angles in neon than in helium. Owing to the tendency for an arc to strike in neon and the consequent difficulty in keeping the thermionic current constant the small peaks at large angles could not be measured accurately and a table similar to that given for helium can not be given for neon. However, the same tendency is observable at the extremes of voltage. At 360 volts the scattering is reduced to one-hundredth its 0° value at about 12°, and at 75 volts it is reduced to the same fraction at about 18°. The tendency towards concentration about the primary beam at high electron velocities is thus evident, but electrons of the same velocity seem to be scattered through larger angles than in the case of helium. In view of the much greater mass of the neon atom this is a tendency which might be expected from purely classical considerations. However, the effect is probably not due entirely to the difference in mass as will be seen when the diatomic gases are considered.

As in helium, the secondary peak increases in relation to the primary peak as larger angles are examined. But there is one rather striking difference between the two gases. Throughout the angular region investigated which in neon was from 0° to 20° the secondary peak, though it increased, always

remained smaller than the primary peak. This is in accord with the well-known fact that in neon the probability of excitation is unusually small in comparison with other gases. This may be accentuated by the fact that those electrons which collide inelastically in neon are deflected through larger angles than in the case of helium. Nitrogen resembles neon in this respect. There is also evidence, from the curves, of a group of electrons which have suffered two inelastic collisions. These appear at a lower voltage than in helium as would be expected from the difference in the radiating potentials of the two gases.

The general picture of the scattering is thus the same as in helium. However, the elastically scattered electrons of the same voltage are deflected through larger angles in neon. This is still more true of the inelastically scattered electrons. The same tendency to concentrate about the primary beam with increased voltage was observable in neon.

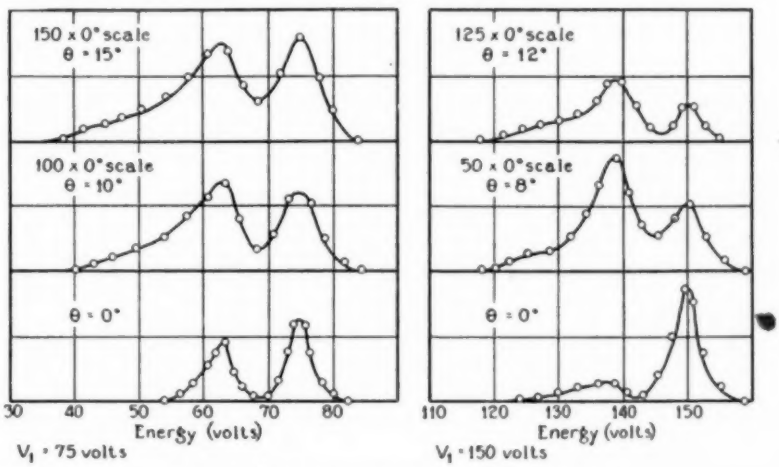

Fig. 3. Typical scattering curves for H_2.

Hydrogen.—The first diatomic gas investigated was hydrogen, and as can be seen from Fig. 3 the results differ in several respects from those obtained in helium. This is particularly so for the scattering at 0°. The curve obtained for 100 volt electrons is strikingly similar to the photometer curve given by Jones and Whiddington.[2] Most of the electrons which enter the analyser have lost no energy. There is a peak corresponding to the loss of enough energy to excite the hydrogen molecule and there is also some evidence of electrons which have suffered two inelastic collisions. The mean difference between the peaks of a large number of curves is 12.3 volts which is in good agreement with the value of 12.26 obtained by Jones and Whiddington. Their results can only be compared with the 0° curves as they had no method of investigating other angles.

The angular scattering of the electrons which have collided elastically is very similar to that observed in helium. The accuracy is not sufficient to establish definitely whether they are deflected through smaller angles than in helium, but they are certainly not deflected through larger angles. This is in a general way what would be expected classically from the difference in

mass between the hydrogen molecule and helium atom. This similarity however, does not apply to the secondary peaks.

The most striking difference is seen to be at 0°; for here, at all voltages used the secondary peak is very much larger than in helium or neon. This is perhaps related to the fact that a larger number of ions is formed per centimeter in hydrogen than in helium. This effect should be greater at low voltages as is seen to be the case, but even at 75 volts only three times as many ionizing collisions are made per centimeter in hydrogen as in helium. The factor at these low voltages as given by these curves is very much larger than this, so that it is unlikely that the effect is due entirely to this cause. The conclusion is then that an electron which collides inelastically, has a better chance of being undeflected or of being deflected only through a fraction of a degree if the collision takes place with a hydrogen molecule than if it is with a helium atom. The voltages used are well above any of the critical potentials so in all probability the difference in the values of these potentials in the two gases is not directly the cause of this difference in behavior. It may be connected with the fact that the hydrogen is in the molecular state and the results obtained in nitrogen lend some support to this view. The general behavior of the secondary peak with variation in angle and voltage is the same as in the monatomic gases; but its rate of decrease with angle is less than in either of the other gases which have been discussed. At 75 volts the secondary peak decreases more rapidly with angle than the primary peak. However, for voltage above 75 the secondary peak definitely becomes much larger than the primary peak. This can be seen at 100 volts and is still more strikingly so at 150 volts. The behavior above 200 volts is not as regular as in the preceding gases. The probable cause of this is the complication introduced by the large number of electrons which have suffered two or more inelastic collisions. At these high voltages the peaks broaden out and as they are close together in hydrogen the analysis becomes difficult.

As would be expected electrons which have lost twice the energy necessary to excite radiation appear at much lower voltages than in helium or neon. Their number is small but larger in proportion than in the other two gases. The distribution of these in angle is a little uncertain, but they appear to have the distribution which would be expected if the second collision had the same deflecting effect as the first.

Nitrogen.—The behavior of electrons in nitrogen shows many points of similarity with the cases previously discussed. The mean distance between the primary and secondary peaks is 12.9 volts. This is a slightly greater value than was observed in hydrogen as would be expected in view of the excitation potentials of nitrogen. In none of the cases is the resolution sufficient to distinguish between the various excitation potentials. The secondary peaks are rather broad, indicating that more than one of these contribute. This would be expected from the band-like character of the nitrogen excitation spectrum.[7] The amount of the peak due to each of the various radiating potentials can not be ascertained.

The scattering of the electrons which have only collided elastically resembles very closely that observed in neon. The most probable angle at

[7] Brandt, Zeits. f. Physik **8**, 32 (1921).

which these electrons are scattered is even a little larger than in the case of neon which was in turn considerably greater than for helium or hydrogen. This again is a result which might be expected from purely classical momentum considerations, though the agreement may be merely fortuitous. The tendency of these electrons to concentrate in the solid angles close to the original beam as their velocity increases is also present, but as in hydrogen this is not so marked as in the rare gases. It seems even less evident than in the case of hydrogen. The reason for this variation with voltage and for the difference in the behavior of the gases is rather obscure and is a point upon which further investigation is in progress.

At 0° the secondary peak is more prominent than in helium or neon but less so than in hydrogen. The number of collisions per centimeter resulting in radiation in nitrogen is probably much greater than in hydrogen, so it must be presumed that at a radiating collision there is a much greater probability of deflection than in hydrogen.

The variation in the ratio of the two peaks with angle is much the same as in the previous cases. The primary peak diminishes much more rapidly than the secondary one. But, as in the case of neon, as far as 20° the primary peak is still the larger. As in hydrogen the peak representing those electrons which have suffered two inelastic collisions occurs at quite a low voltage. The variation with angle and voltage is much the same as in the case of hydrogen.

Thus the behavior of the scattered electrons in nitrogen has certain points in common with that observed in both neon and hydrogen. As in the case of neon, which also has a large mass, there is a tendency for both primary and secondary electrons to be scattered through larger angles than in helium or hydrogen. But in common with hydrogen there seems to be quite a large probability for an electron to sustain an inelastic collision without deflection. This is not so marked, however, as in the case of hydrogen.

The cases which have so far been discussed are all for electrons with energies equal to or greater than 75 volts. This voltage was chosen as the minimum, as it was well above the point at which the complications which would be expected in the neighborhood of the critical potentials, would become evident. The gases used were chosen as being easily obtainable and representative of monatomic and diatomic molecules. Mercury vapor and atomic hydrogen are also of considerable interest but so far the work with these gases is only in its preliminary stages. The region below 75 volts is one of great interest and it has been investigated in some detail in helium and hydrogen. However, the results obtained have not been sufficiently established to be presented at this time.

In conclusion, it is a pleasure to express my indebtedness to the National Research Council for its support, to Princeton University for the facilities so kindly placed at my disposal, and to Professor K. T. Compton for his helpful criticism and advice throughout this work.

PALMER PHYSICAL LABORATORY,
PRINCETON, NEW JERSEY,
December 20, 1928.

RELATIVITY PRECESSION

By Leigh Page

Abstract

An expression has been deduced for the time rate of change of a vector relative to a basic inertial system S in terms of the time rate of change of the vector relative to the inertial system S' in which its origin is momentarily at rest.

Assuming the vector to remain constant in direction and magnitude relative to the system in which its origin is momentarily at rest, the change of the vector relative to the basic inertial system has been investigated under the following headings: (*a*) Deformation of a small closed surface; (*b*) Vector moving in a plane; (*c*) Motion in a circle; (*d*) Classical Keplerian motion; (*e*) Relativity Keplerian motion; particular attention being paid to the mean rate of precession of the vector.

Assuming the vector to have an angular velocity without change of magnitude relative to the inertial system in which its origin is momentarily at rest, the angular velocity and rate of change of magnitude relative to the basic inertial system have been calculated. As a check on the formula the angular velocity of the lines of force of a moving point charge has been computed.

IN DEVELOPING the theory of the spinning electron Thomas[1] has investigated the rotation relative to a basic inertial system S (the system in which the nucleus is at rest) of a vector attached to an electron which has a finite velocity $\boldsymbol{v}$ and acceleration $\boldsymbol{f}$ relative to S, the vector under consideration having a known angular velocity relative to the system S' in which the electron is momentarily at rest. Thomas' method depends on the fact that if two systems S' and S'' have velocities $\boldsymbol{v}$ and $\boldsymbol{v}+\delta\boldsymbol{v}$ relative to S, then a Lorentz transformation from S to S'' is equivalent to a Lorentz transformation from S to S', followed by a rotation through the angle

$$(1-k)\boldsymbol{v}\times\delta\boldsymbol{v}/v^2 \tag{1}$$

in S' and a Lorentz transformation with the velocity

$$k\{\delta\boldsymbol{v}+(k-1)(\boldsymbol{v}\cdot\delta\boldsymbol{v}/v^2)\boldsymbol{v}\} \tag{2}$$

which S'' possesses relative to S', where k (Thomas' β) is given by

$$k\equiv(1-\beta^2)^{-1/2}, \quad \beta\equiv v/c.$$

Thomas' method, however, does not appear to give the rate of rotation of the vector under consideration as it would be measured by an observer stationed in the basic inertial system S.

The object of the present paper is to investigate the change in magnitude and direction relative to an inertial system S of a vector the origin of which has an arbitrary motion relative to S, in terms of the angular velocity and rate of change of magnitude of the vector relative to the inertial system S' in which its origin is momentarily at rest. For this purpose we may consider

[1] L. H. Thomas, Phil. Mag. **3**, 1 (1927).

the vector as a straight line joining two nearby points p and P, the distance between which we can make as small as we choose. As no particular advantage seems to accrue from using four-dimensional vector or tensor analysis we shall employ only three-dimensional space vectors.

Consider an inertial system S' in which the point p is at rest at the origin of coordinates at the time 0. Then at any time t' the position vector of p is

$$\boldsymbol{r}' = \tfrac{1}{2}\boldsymbol{f}'t'^2 + \cdots \quad . \tag{3}$$

where $\boldsymbol{f}'$ is the acceleration of p relative to S'. The higher order terms in the series for $\boldsymbol{r}'$, involving the time derivatives of $\boldsymbol{f}'$, are negligible for our purposes and therefore have not been written down. Similarly the position vector of P at the time t' is

$$\boldsymbol{R}' = \boldsymbol{\varrho}' + \frac{d\boldsymbol{\varrho}'}{dt'}t' + \frac{d^2\boldsymbol{\varrho}'}{dt'^2}t'^2 \cdots + \frac{1}{2}\boldsymbol{f}'t'^2 + \cdots \tag{4}$$

where $\boldsymbol{\varrho}'$ is the vector pP as it appears to observers in S' at the time $t'=0$ when its origin p is at rest in S', and the derivatives of $\boldsymbol{\varrho}'$ represent the time rate of increase etc. of the vector $\boldsymbol{R}'-\boldsymbol{r}'$ relative to S'. All these derivatives will be assumed to be at most of the same order of magnitude as the small quantity $\boldsymbol{\varrho}'$. It might be considered preferable to have made the acceleration $\boldsymbol{f}'$ in Eq. (4) less than that in Eq. (3) by a term of the order of $\boldsymbol{\varrho}'$ so that when $d\boldsymbol{\varrho}'/dt'$ and the higher derivatives of $\boldsymbol{\varrho}'$ vanish the vector $\boldsymbol{R}'-\boldsymbol{r}'$ would suffer the Lorentz contraction as it acquires a velocity relative to S' and therefore would maintain the same constant magnitude relative to the inertial system in which its origin p is momentarily at rest. Such a refinement, however, would change the final result only by the addition of second order terms in the small quantity $\boldsymbol{\varrho}'$ and is therefore of no consequence.

The Lorentz transformations between systems S and S' may be written in the vector form

$$\boldsymbol{r} = \boldsymbol{r}' + \left(\frac{1}{k}-1\right)\frac{\boldsymbol{r}'\cdot\boldsymbol{v}}{v^2}\boldsymbol{v} + \boldsymbol{v}t, \qquad t' = \frac{t}{k} - \frac{\boldsymbol{r}'\cdot\boldsymbol{v}}{c^2}, \tag{5}$$

where, as usual, letters without accents refer to measurements in S and those with primes to measurements in S'.

Let us denote the position vectors of p and P at time $t=0$ by $\boldsymbol{r}_1'$ and $\boldsymbol{R}_1'$ respectively as measured in S' and by $\boldsymbol{r}_1$ and $\boldsymbol{R}_1$ as measured in S, the corresponding times in S' being designated by t_1' and T_1'. Then from Eqs. (3) and (5)

$$t_1' = 0, \qquad \boldsymbol{r}_1' = 0\ ;$$

and from Eqs. (4) and (5)

$$T_1' = -\frac{\boldsymbol{R}_1'\cdot\boldsymbol{v}}{c^2}, \qquad \boldsymbol{R}_1' = \boldsymbol{\varrho}' - \frac{\boldsymbol{R}_1'\cdot\boldsymbol{v}}{c^2}\frac{d\boldsymbol{\varrho}'}{dt'} \cdots + \frac{1}{2}\left(\frac{\boldsymbol{R}_1'\cdot\boldsymbol{v}}{c^2}\right)^2\boldsymbol{f}' + \cdots\ ; \tag{6}$$

where we have retained all terms of the first and second orders in the small quantity $\boldsymbol{\varrho}'$. Using Eq. (5)

$$\boldsymbol{r}_1=0, \quad \boldsymbol{R}_1=\boldsymbol{R}_1'+\left(\frac{1}{k}-1\right)\frac{\boldsymbol{R}_1'\cdot\boldsymbol{v}}{v^2}\boldsymbol{v}.$$

The vector or directed line pP as observed from S at the time $t=0$ is therefore

$$\boldsymbol{\varrho}_1=\boldsymbol{R}_1-\boldsymbol{r}_1=\boldsymbol{R}_1'+\left(\frac{1}{k}-1\right)\frac{\boldsymbol{R}_1'\cdot\boldsymbol{v}}{v^2}\boldsymbol{v} \tag{7}$$

where $\boldsymbol{R}_1'$ is specified by Eq. (6).

Similarly if the subscript 2 is used to designate quantities measured at the time $t=dt$ we find

$$\begin{gathered} t_2'=dt/k, \qquad \boldsymbol{r}_2'=0\ ; \\ T_2'=\frac{dt}{k}-\frac{\boldsymbol{R}_2'\cdot\boldsymbol{v}}{c^2}, \quad \boldsymbol{R}_2'=\boldsymbol{\varrho}'+\left(\frac{dt}{k}-\frac{\boldsymbol{R}_2'\cdot\boldsymbol{v}}{c^2}\right)\frac{d\boldsymbol{\varrho}'}{dt'} \\ \cdots+\frac{1}{2}\left(\frac{dt}{k}-\frac{\boldsymbol{R}_2'\cdot\boldsymbol{v}}{c^2}\right)^2\boldsymbol{f}'+\cdots\ ; \end{gathered} \tag{8}$$

and using Eq. (5) again the directed line pP as observed from S at the time $t=dt$ is seen to be given in magnitude and direction by

$$\boldsymbol{\varrho}_2=\boldsymbol{R}_2-\boldsymbol{r}_1=\boldsymbol{R}_2'+\left(\frac{1}{k}-1\right)\frac{\boldsymbol{R}_2'\cdot\boldsymbol{v}}{v^2}\boldsymbol{v}, \tag{9}$$

where $\boldsymbol{R}_2'$ is specified by Eq. (8).

The increase in the vector $\boldsymbol{\varrho}_1$ occurring in the time dt is therefore

$$d\boldsymbol{\varrho}=\boldsymbol{\varrho}_2-\boldsymbol{\varrho}_1=\boldsymbol{R}_2'-\boldsymbol{R}_1'+\left(\frac{1}{k}-1\right)\frac{(\boldsymbol{R}_2'-\boldsymbol{R}_1')\cdot\boldsymbol{v}}{v^2}\boldsymbol{v} \tag{10}$$

Subtracting Eq. (6) from (8) and retaining only first order terms in $\boldsymbol{\varrho}'$,

$$\boldsymbol{R}_2'-\boldsymbol{R}_1'=\left\{\frac{d\boldsymbol{\varrho}'}{dt'}-\frac{\boldsymbol{\varrho}'\cdot\boldsymbol{v}}{c^2}\boldsymbol{f}'\right\}\frac{dt}{k}.$$

So Eq. (10) becomes

$$\frac{d\boldsymbol{\varrho}}{dt}=\frac{1}{k}\left\{\frac{d\boldsymbol{\varrho}'}{dt'}+\left(\frac{1}{k}-1\right)\frac{d\boldsymbol{\varrho}'}{dt'}\cdot\boldsymbol{v}\frac{\boldsymbol{v}}{v^2}\right\}-\frac{\boldsymbol{\varrho}'\cdot\boldsymbol{v}}{kc^2}\left\{\boldsymbol{f}'+\left(\frac{1}{k}-1\right)\frac{\boldsymbol{f}'\cdot\boldsymbol{v}}{v^2}\boldsymbol{v}\right\}. \tag{11}$$

If $\boldsymbol{f}$ is the acceleration of p as measured in S then

$$\boldsymbol{f}=\frac{1}{k^2}\left\{\boldsymbol{f}'+\left(\frac{1}{k}-1\right)\frac{\boldsymbol{f}'\cdot\boldsymbol{v}}{v^2}\boldsymbol{v}\right\},$$

and from Eq. (7) and (6)

$$\boldsymbol{\varrho}\cdot\boldsymbol{v}=\frac{1}{k}\boldsymbol{R}'\cdot\boldsymbol{v}=\frac{1}{k}\boldsymbol{\varrho}'\cdot\boldsymbol{v}.$$

Consequently Eq. (11) may be written

$$\frac{d\varrho}{dt}=\frac{1}{k}\left\{\frac{d\varrho'}{dt'}+\left(\frac{1}{k}-1\right)\frac{d\varrho'}{dt'}\cdot v\frac{v}{v^2}\right\}-k^2\frac{\varrho\cdot v}{c^2}f. \tag{12}$$

If the vector ϱ' maintains a constant direction and magnitude relative to the system in which its origin p is momentarily at rest, then $d\varrho'/dt'=0$, and the rate of change of the vector relative to the basic inertial system S is given by

$$\frac{d\varrho}{dt}=-k^2\frac{\varrho\cdot v}{c^2}f\cdot \tag{13}$$

We shall consider several applications of (13) before returning to the more general equation (12).

Deformation of Small Closed Surface

Consider a small closed surface and designate some point in its interior as center. We shall suppose that relative to the inertial system in which its center is momentarily at rest the surface has no motion either of rotation or of distortion with respect to its center. Then if we denote by ϱ the position vector of a point on the surface relative to its center as origin, we may use Eq. (13) which may be written in the form

$$\frac{d\varrho}{dt}=-\frac{k^2}{2c^2}(fv+vf)\cdot\varrho-\frac{k^2}{2c^2}(v\times f)\times\varrho, \tag{14}$$

where v and f represent the velocity and acceleration of the center of the surface. The second term represents a rotation of the surface relative to S with angular velocity

$$\omega=-\frac{k^2}{2c^2}v\times f, \tag{15}$$

while the first represents a symmetric distortion or pure strain. If we take XY axes in the plane of v and f with the X axis bisecting the angle θ between these two vectors the dyadic appearing in the first term of (14) may be written

$$-\frac{k^2}{2c^2}(fv+vf)=-\frac{k^2vf}{c^2}\left(ii\,\cos^2\frac{\theta}{2}-jj\sin^2\frac{\theta}{2}\right)$$

showing that the axes of distortion coincide with the coordinate axes. A radius vector parallel to the X axis is shortened by the acceleration, whereas, one parallel to the Y axis is lengthened, dimensions parallel to the Z axis being unaffected. At the same time the surface as a whole rotates about the Z axis with the angular velocity (15), that is, in the sense f to v.

As a check on the formula (13) or (14) suppose that the closed surface under consideration is a sphere of radius a relative to the system in which its center is momentarily at rest. Then on account of the Fitzgerald-Lorentz contraction it should appear in S as an oblate spheroid of short axis a/k in the direction of v at the time 0 and as an oblate spheroid of short axis

$$\frac{a}{k}\left(1-k^2\frac{\mathbf{v}\cdot\mathbf{f}}{c^2}dt\right)$$

in the direction of the vector $\mathbf{v}+\mathbf{f}dt$ at the time dt. We shall show that (14) transforms the first of these oblate spheroids into the second.

Let $\mathbf{a}$ be a vector of constant magnitude a and variable direction. Take the X axis in the direction of $\mathbf{v}$ and orient the YZ axes so that $\mathbf{f}$ lies in the XY plane making an angle θ with $\mathbf{v}$. Then the equation of the first spheroid is

$$\varrho_1=((1/k)\mathbf{ii}+\mathbf{jj}+\mathbf{kk})\cdot\mathbf{a}.$$

Referred to these axis (13) takes the form

$$\frac{d\varrho}{dt}=-k^2\frac{vf}{c^2}(\mathbf{ii}\cos\theta+\mathbf{ji}\sin\theta)\cdot\varrho_1$$

$$=-k\frac{vf}{c^2}(\mathbf{ii}\cos\theta+\mathbf{ji}\sin\theta)\cdot\mathbf{a}.$$

Therefore the equation of the second spheroid is

$$\varrho_2\equiv\varrho_1+(d\varrho/dt)dt=\left[\frac{1}{k}\left(1-k^2\frac{vf\cos\theta dt}{c^2}\right)\mathbf{ii}-k\frac{vf\sin\theta dt}{c^2}\mathbf{ji}+\mathbf{jj}+\mathbf{kk}\right]\cdot\mathbf{a}.$$

If, now, we refer this equation to a set of axes $X_1Y_1Z_1$ obtained from XYZ by a rotation in the XY plane through the angle whose tangent is $f\sin\theta\,dt/v$ we have

$$\mathbf{i}=\mathbf{i}_1-\mathbf{j}_1(f/v)\sin\theta dt,$$

$$\mathbf{j}=\mathbf{i}_1(f/v)\sin\theta dt+\mathbf{j}_1,$$

and referred to the new axes

$$\varrho_2=\left[\frac{1}{k}\left(1-k^2\frac{\mathbf{v}\cdot\mathbf{f}}{c^2}dt\right)\mathbf{i}_1\mathbf{i}_1+\mathbf{j}_1\mathbf{j}_1+\mathbf{kk}\right]\cdot\left[\mathbf{a}+(1-k)\frac{(\mathbf{v}\times\mathbf{f}dt)\times\mathbf{a}}{v^2}\right].$$

If we put

$$\mathbf{b}\equiv\mathbf{a}+(1-k)(\mathbf{v}\times\mathbf{f}dt)\times\mathbf{a}/v^2$$

$\mathbf{b}$ is a unit vector which has been formed from $\mathbf{a}$ by a rotation

$$(1-k)\mathbf{v}\times\mathbf{f}dt/v^2$$

equal to that specified by Eq. (1). Therefore

$$\varrho_2=\left[\frac{1}{k}\left(1-k^2\frac{\mathbf{v}\cdot\mathbf{f}}{c^2}dt\right)\mathbf{i}_1\mathbf{i}_1+\mathbf{j}_1\mathbf{j}_1+\mathbf{kk}\right]\cdot\mathbf{b}$$

is the equation of an oblate spheroid with short axis in the direction of the vector $\mathbf{v}+\mathbf{f}dt$ and with axes of the expected magnitudes. It is interesting in this connection to note that, as the velocity changes in direction, a point on the spheroid lying on the forward pole of the short axis does not rotate from the direction of the original velocity toward that of the increased velocity, as a casual inspection of the problem might suggest, but, as the formula (15) indicates, in precisely the opposite direction.

Vector Moving in a Plane

Now we shall consider the rotation and change in magnitude relative to the basic system S of a vector or directed line element the origin of which has an arbitrary motion in a plane, the vector remaining at all times constant in direction and magnitude relative to the inertial system in which its origin is momentarily at rest.

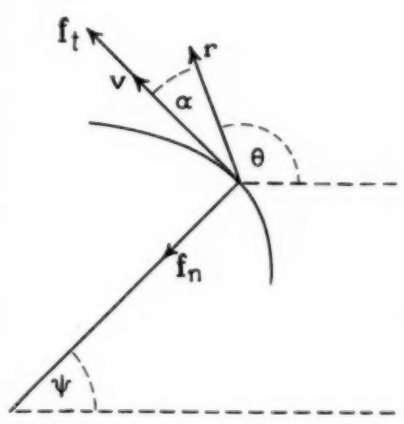

Fig. 1.

Let the plane of the paper (Fig. 1) represent the plane of the motion relative to S, f_t and f_n being the tangential and normal components of the acceleration $\boldsymbol{f}$. Eq. (13) shows that the component of the vector perpendicular to the plane of the motion remains constant: we may therefore confine our attention to the component $\boldsymbol{r}$ of $\boldsymbol{\varrho}$ lying in the plane of the figure, writing (13) in the form

$$d\boldsymbol{r}/dt = -k^2\boldsymbol{r}\cdot\boldsymbol{v}\boldsymbol{f}/c^2 \tag{16}$$

If we denote by θ the angle which $\boldsymbol{r}$ makes with some fixed direction in the plane of the motion and by ψ the angle which the normal to the curve described by the moving vector makes with the same direction,

$$\frac{d\theta}{dt} = \frac{1}{r^2}\left|\boldsymbol{r}\times\frac{d\boldsymbol{r}}{dt}\right| = -\frac{k^2}{r^2}\,\frac{\boldsymbol{r}\cdot\boldsymbol{v}}{c^2}\left|\boldsymbol{r}\times\boldsymbol{f}\right| .$$

But

$$f_t = dv/dt, \quad f_n = vd\psi/dt.$$

Therefore

$$d\theta/dt = -k^2\beta^2\cos^2\alpha d\psi/dt - k^2\beta\sin\alpha\cos\alpha d\beta/dt,$$

where α is the angle between $\boldsymbol{r}$ and $\boldsymbol{v}$.

If we eliminate θ by means of the relation

$$d\theta/dt = d\psi/dt - d\alpha/dt,$$

we get

$$\frac{d\psi}{dt} = \frac{1-\beta^2}{1-\beta^2\sin^2\alpha}\,\frac{d\alpha}{dt} - \frac{\beta\sin\alpha\cos\alpha}{1-\beta^2\sin^2\alpha}\,\frac{d\beta}{dt} \tag{17}$$

and integrating

$$\tan^{-1}((1-\beta^2)^{1/2}\tan\alpha) = \int (1-\beta^2)^{-1/2}d\psi . \tag{18}$$

Therefore α increases by 2π and the vector returns to the same orientation relative to the velocity $\boldsymbol{v}$ when ψ increases by the amount specified by the equation

$$\int (1-\beta^2)^{-1/2}d\psi = 2\pi . \tag{19}$$

To find the change in magnitude of the moving vector we have

$$\frac{1}{r}\frac{dr}{dt}=\frac{1}{r^2}\mathbf{r}\cdot\frac{d\mathbf{r}}{dt}=-\frac{k^2}{r^2}\frac{\mathbf{r}\cdot\mathbf{v}}{c^2}\mathbf{r}\cdot\mathbf{f}$$

$$=k^2\beta^2\sin\alpha\cos\alpha\frac{d\psi}{dt}-k^2\beta\cos^2\alpha\frac{d\beta}{dt}.$$

Eliminating ψ by means of (17) we get

$$\frac{1}{r}\frac{dr}{dt}=\frac{\beta^2\sin\alpha\cos\alpha}{1-\beta^2\sin^2\alpha}\frac{d\alpha}{dt}+\frac{\beta\sin^2\alpha}{1-\beta^2\sin^2\alpha}\frac{d\beta}{dt}-\frac{\beta}{1-\beta^2}\frac{d\beta}{dt}, \tag{20}$$

and integrating

$$r=r_0\left(\frac{1-\beta^2}{1-\beta^2\sin^2\alpha}\right)^{1/2} \tag{21}$$

This equation confirms our expectation that when $\mathbf{r}$ is perpendicular to $\mathbf{v}$ it has the same magnitude r_0 independent of the velocity with which it may be moving, and that when it is parallel to $\mathbf{v}$ it suffers the Fitzgerald-Lorentz contraction and appears shortened in the ratio $(1-\beta^2)^{1/2}:1$.

We shall now take up a few applications which are of interest in connection with atomic dynamics.

Motion in a Circle

If the vector $\boldsymbol{\rho}$ is revolving in a circle with constant speed (18) gives

$$\tan\alpha=(1-\beta^2)^{-1/2}\tan k\Omega t, \tag{22}$$

where Ω is the angular velocity of revolution. Differentiating

$$\frac{d\alpha}{dt}=\frac{\Omega}{1-\beta^2\cos^2 k\Omega t},$$

and the angular velocity of $\boldsymbol{\rho}$ about the normal to the plane of the orbit is

$$\frac{d\theta}{dt}=\Omega-\frac{d\alpha}{dt}=-\frac{\beta^2\cos^2 k\Omega t}{1-\beta^2\cos^2 k\Omega t}\Omega, \tag{23}$$

the negative sign indicating that $\boldsymbol{\rho}$ rotates in the opposite sense to that of revolution. To get the mean angular velocity of $\boldsymbol{\rho}$ during a complete rotation of the vector we may find the average value of this expression during the time $1/(k\Omega)$ or more simple we obtain at once from (19)

$$d\alpha/dt=k\Omega,$$

and therefore

$$\overline{d\theta}/dt=\Omega-\overline{d\alpha}/dt=-(k-1)\Omega. \tag{24}$$

The magnitude of the projection of $\boldsymbol{\rho}$ on the plane of the motion is given by (21). Eliminating α by means of (22)

$$r=r_0(1-\beta^2\cos^2 k\Omega t)^{1/2}. \tag{25}$$

Classical Keplerian Motion

We shall suppose that the vector ϱ is attached to a particle (such as an electron) which is describing an orbit under an inverse square force of attraction directed toward a fixed point in S chosen as origin of polar coordinates r and ϕ. The vector ϱ will be supposed to maintain a constant direction and magnitude relative to the inertial system in which the particle is momentarily at rest. We wish to find the mean rate of rotation of ϱ relative to the basic system S. As the component of ϱ perpendicular to the plane of revolution is unaltered by the motion we shall not limit the generality of our result if we assume ϱ to lie in this plane.

If we designate by χ the angle between the radius vector and the normal to the orbit (Fig. 2) we have

$$d\psi = d\phi - d\chi, \qquad \tan\chi = (1/r)(dr/d\phi), \tag{26}$$

where ψ has the same significance as previously.

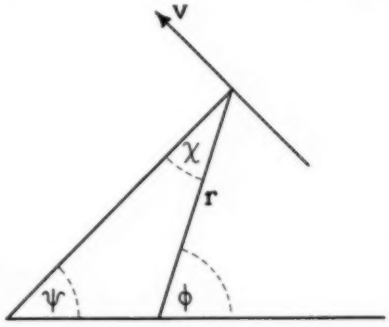

Fig. 2.

In our present discussion we shall assume the Newtonian dynamics. The orbit, therefore, is a stationary ellipse given by the equation

$$\frac{1}{r} = \frac{1+\epsilon\cos\phi}{a(1-\epsilon^2)}, \tag{27}$$

a being the semi-major-axis and ϵ the eccentricity. Eliminating r and χ,

$$d\psi = \frac{1+\epsilon\cos\phi}{1+2\epsilon\cos\phi+\epsilon^2}\,d\phi.$$

The energy equation is

$$U = \frac{1}{2}mv^2 - \frac{g}{r} = -\frac{g}{2a} = -\frac{mg^2}{2p^2}(1-\epsilon^2), \tag{28}$$

where U is the total energy, the constant g has been put for e^2Z in the usual notation, and p represents the constant angular momentum of revolution of the particle. Using the equation of the orbit to eliminate r

$$\frac{1}{2}\beta^2 = \frac{g^2}{2p^2c^2}(1+2\epsilon\cos\phi+\epsilon^2).$$

In the present discussion we shall confine ourselves to a first approximation so as to avoid the irrationality involved in the denominator of the right-hand member of (18). We have then

$$\int (1-\beta^2)^{-1/2}d\psi = \int d\psi\left(1+\frac{1}{2}\beta^2\cdots\right)$$

$$= \int \frac{1+\epsilon\cos\phi}{1+2\epsilon\cos\phi+\epsilon^2}\,d\phi + \frac{g^2}{2p^2c^2}\int (1+\epsilon\cos\phi)d\phi.$$

Performing the integration (18) becomes

$$\tan^{-1}((1-\beta^2)^{1/2}\tan\alpha)=\tan^{-1}\left(\frac{\sin\phi}{\cos\phi+\epsilon}\right)+\frac{g^2}{2p^2c^2}(\phi+\epsilon\sin\phi) \tag{29}$$

To find the mean angular velocity of the vector ϱ let ϕ increase by $2\pi n$, n being chosen so that the corresponding increase in α is $2\pi(n+1)$. Then the equation above shows that

$$n=2p^2c^2/g^2.$$

Since α is the angle which ϱ makes with v, n represents the number of revolutions of the particle necessary for ϱ to make one complete rotation relative to S in the sense opposite to the revolution. Therefore the mean rotation of ϱ per revolution is

$$\Delta\theta=-2\pi/n=-\pi g^2/p^2c^2=-\pi e^4Z^2/p^2c^2, \tag{30}$$

which is equal (to the degree of approximation here employed) to the advance of the perihelion of an elliptical orbit per revolution as calculated by Sommerfeld on the relativity theory.

Relativity Keplerian Motion

Now we shall treat the problem just investigated using the relativity dynamics in place of the Newtonian dynamics. As the velocity appears in the energy equation in the form $(1-\beta^2)^{1/2}$ we shall be able to obtain an exact expression for the mean angular velocity of the vector ϱ relative to S without being forced to the approximations involved in the previous treatment based on the Newtonian dynamics.

Equations (26) hold as before, but (27) must be replaced by

$$\frac{1}{r}=\frac{1+\epsilon\cos\gamma\phi}{a(1-\epsilon^2)}, \tag{31}$$

where

$$\gamma^2\equiv 1-g^2/p^2c^2.$$

If we eliminate r and χ between (26) and (31) and put μ for $\gamma\phi$

$$d\psi=\frac{1}{\gamma}\,\frac{(1+\epsilon\cos\mu)\{1+\epsilon(1-\gamma^2)\cos\mu\}d\mu}{(1+\epsilon^2\gamma^2)+2\epsilon\cos\mu+\epsilon^2(1-\gamma^2)\cos^2\mu}.$$

The energy equation for this case is

$$U=\frac{mc^2}{(1-\beta^2)^{1/2}}-\frac{g}{r}=\frac{g\gamma^2}{a(1-\gamma^2)(1-\epsilon^2)}=\frac{\gamma mc^2}{[1-\epsilon^2(1-\gamma^2)]^{1/2}} \tag{32}$$

where m is the rest mass of the revolving particle. Using the equation of the orbit (31) to eliminate r,

$$\frac{1}{(1-\beta^2)^{1/2}}=\frac{U}{mc^2\gamma^2}\{1+\epsilon(1-\gamma^2)\cos\mu\}.$$

Therefore

$$\int \frac{d\psi}{(1-\beta^2)^{1/2}} = \frac{U}{mc^2\gamma^3} \int \frac{(1+\cos\mu)\{1+\epsilon(1-\gamma^2)\cos\mu\}^2 d\mu}{(1+\epsilon^2\gamma^2)+2\epsilon\cos\mu+\epsilon^2(1-\gamma^2)\cos^2\mu}$$

$$= \frac{U}{mc^2\gamma^3}\Bigg[(1-\gamma^2)\int (1+\epsilon\cos\mu)d\mu$$

$$+\gamma^2\{1-\epsilon^2(1-\gamma^2)\}\int \frac{(1+\epsilon\cos\mu)d\mu}{(1+\epsilon^2\gamma^2)+2\epsilon\cos\mu+\epsilon^2(1-\gamma^2)\cos^2\mu}\Bigg]. \qquad (33)$$

We shall integrate through a complete revolution of μ, that is, from one perihelion to the next. If we put

$$z=e^{i\mu}, \qquad d\mu=-idz/z, \qquad \cos\mu=(z^2+1)/2z,$$

then the complex quantity z describes a unit circle about the origin as μ increases from 0 to 2π. In terms of z the second integral in (33) becomes

$$I \equiv \int_0^{2\pi} \frac{(1+\epsilon\cos\mu)d\mu}{(1+\epsilon^2\gamma^2)+2\epsilon\cos\mu+\epsilon^2(1-\gamma^2)\cos^2\mu}$$

$$= -\frac{2i}{\epsilon^2(1-\gamma^2)} \oint \frac{(\epsilon z^2+2z+\epsilon)dz}{(z-z_1)(z-z_2)(z-z_3)(z-z_4)}$$

where

$$z_1 \equiv -\frac{1+(1-\epsilon^2(1-\gamma^2))^{1/2}}{\epsilon(1-\gamma)}, \qquad z_3 \equiv -\frac{1-(1-\epsilon^2(1-\gamma^2))^{1/2}}{\epsilon(1-\gamma)},$$

$$z_2 \equiv -\frac{1+(1-\epsilon^2(1-\gamma^2))^{1/2}}{\epsilon(1+\gamma)}, \qquad z_4 \equiv -\frac{1-(1-\epsilon^2(1-\gamma^2))^{1/2}}{\epsilon(1+\gamma)}.$$

The positions of the poles of the integrand are illustrated in Fig. 3. As z_3 and z_1 are the only poles lying within the unit circle the path of integration

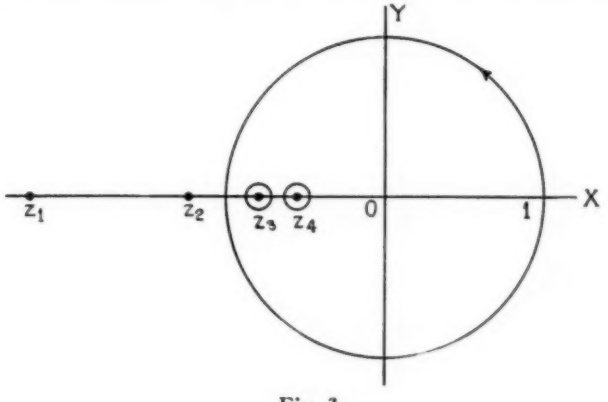

Fig. 3.

may be replaced by two small circles about these poles and the integral becomes the product of $2\pi i$ by the sum of the residues of the integrand at these two poles, that is,

$$I = \frac{4\pi}{\epsilon^2(1-\gamma^2)}\left[\frac{\epsilon z_3^2+2z_3+\epsilon}{(z_3-z_1)(z_3-z_2)(z_3-z_4)} + \frac{\epsilon z_4^2+2z_4+\epsilon}{(z_4-z_1)(z_4-z_2)(z_4-z_3)}\right]$$

$$= \frac{2\pi}{(1-\epsilon^2(1-\gamma^2))^{1/2}}.$$

Consequently (33) becomes

$$\int \frac{d\psi}{(1-\beta^2)^{1/2}} = \frac{U}{mc^2\gamma^3}[2\pi(1-\gamma^2)+2\pi\gamma^2(1-\epsilon^2(1-\gamma^2))^{1/2}] \\ = 2\pi+\frac{2\pi U}{mc^2}\,\frac{1-\gamma^2}{\gamma^3} \tag{34}$$

in view of (32).

If, then, n is the number of revolutions of μ necessary for α to increase by $2\pi(n+1)$, it follows from (18) that

$$n=\frac{mc^2}{U}\,\frac{\gamma^3}{1-\gamma^2}\,.$$

The mean increase in α per revolution of μ is therefore

$$\Delta\alpha=2\pi(1+1/n)\,.$$

During one revolution of μ the angle ψ increases by the same amount as the azimuth ϕ, that is, $\Delta\psi=2\pi/\gamma$.

Therefore the vector ϱ rotates through the angle

$$\Delta\theta=\Delta\psi-\Delta\alpha=2\pi\left(\frac{1}{\gamma}-1-\frac{1}{n}\right) \\ =-2\pi\left(\frac{1}{\gamma}-1\right)\left\{\frac{U}{mc^2}\,\frac{\gamma+1}{\gamma^2}-1\right\}. \tag{35}$$

To a first approximation $\gamma=1$ and $U=mc^2$, giving

$$\Delta\theta=-2\pi(1/\gamma-1)=-\pi e^4Z^2/p^2c^2$$

in agreement with the result (30) obtained on the Newtonian dynamics. In cases where γ differs appreciably from unity, however, the dependence of $\Delta\theta$ upon the principal quantum number as well as upon the azimuthal quantum number becomes important.

The rotation of the vector ϱ per revolution of the particle, that is, per revolution of the azimuth ϕ, is obtained by multiplying (35) by γ.

Rotation Relative to Rest System

We shall now return to the more general Eq. (12) which specifies the rate of change relative to the basic system S of a vector whose direction and magnitude are changing relative to the inertial system in which its origin is momentarily at rest. Furthermore, we shall assume that the change in the vector relative to the system S' in which its origin is momentarily at rest is one of pure rotation with angular velocity ω' about an axis perpendicular to the vector without change in magnitude. Then

$$d\varrho'/dt'=\omega'\times\varrho', \qquad \omega'\cdot\varrho'=0,$$

and the time rate of change of the vector in S given by (12) is

$$\frac{d\varrho}{dt}=\frac{1}{k}\left\{\omega'\times\varrho'+\left(\frac{1}{k}-1\right)\omega'\times\varrho'\cdot v\frac{v}{v^2}\right\}-k^2\frac{\varrho\cdot v}{c^2}f.$$

As

$$\varrho=\varrho'+\left(\frac{1}{k}-1\right)\frac{\varrho'\cdot v}{v^2}v$$

we find that the angular velocity ω of ϱ in S about an axis perpendicular to the vector is given by

$$\rho^2\omega=\varrho\times\frac{d\varrho}{dt}=\frac{\rho'^2}{k^2}\left\{\omega'+(k-1)\frac{\omega'\cdot v}{v^2}v\right\}-k^2\frac{\varrho\cdot v}{c^2}\varrho\times f, \tag{36}$$

or

$$\omega=\frac{1}{k^2}\left(1+k^2\frac{\overline{\varrho\cdot v}^2}{\rho^2c^2}\right)\left\{\omega'+(k-1)\frac{\omega'\cdot v}{v^2}v\right\}-\frac{k^2}{\rho^2c^2}\{v\times(\varrho\times f)\}\times\varrho. \tag{37}$$

The first term represents the angular velocity in S due to the angular velocity ω' in S' and the second the angular velocity in S due to the acceleration of the vector. If the vector were rotating in S' without acceleration of its origin the second term would be absent.

The rate of increase of the magnitude of the vector in S is easily found to be

$$\frac{d\rho}{dt}=\frac{1}{\rho}\left(\varrho\cdot\frac{d\varrho}{dt}\right)=-\frac{\varrho\cdot v}{\rho}\left\{\frac{\omega'\times\varrho\cdot v}{c^2}+k^2\frac{\varrho\cdot f}{c^2}\right\}. \tag{38}$$

As a check on formula (37) we shall calculate the rate of rotation relative to S of the lines of electric force of a point charge which has velocity v and acceleration f. The angular velocity of the lines of force relative to the system S' in which the charge is momentarily at rest is[2]

$$\omega'=-\frac{f'\times c'}{c^2}=-\frac{k^2}{c^2\left(1-\frac{c\cdot v}{c^2}\right)}\left\{f\times(c-v)+\left(\frac{1}{k}-1\right)\frac{f\times(c-v)\cdot v}{v^2}v\right\} \tag{39}$$

where c' and c are the velocities relative to S' and S of the moving elements of which the lines of force are the loci. Now the vector ϱ' specifying the direction in which the line of force under consideration leaves the point charge in S' has the direction of c'. So if we put $\varrho'=c'$, then

$$\varrho=c'+\left(\frac{1}{k}-1\right)\frac{c'\cdot v}{v^2}v=\frac{c-v}{k\left(1-\frac{c\cdot v}{c^2}\right)} \tag{40}$$

specifies the direction in which the same line of force leaves the charge as viewed from S.

Furthermore

$$\frac{1}{k^2}\rho^2c^2+\overline{\varrho\cdot v}^2=\frac{c^4}{k^2}. \tag{41}$$

Substituting (39), (40) and (41) in (37) and reducing

$$\omega=-\frac{k^2}{c^2}f\times(c-v) \tag{42}$$

which agrees with the expression[3] deduced on the emission theory.

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YALE UNIVERSITY,
January 7, 1929.

[2] L. Page, Introduction to Electrodynamics p. 27.
[3] L. Page, Am. Jour. Sci. **38**, 176 (1914)

REFRACTIVE INDEX OF SODIUM VAPOR AND WIDTH OF D_1 IN ABSORPTION

By S. A. Korff

Abstract

Continuing the study by Stewart and Korff of the refractive index of sodium vapor near the D lines, more accurate measurements are obtained. The variation of refractive index is found to agree with the classical formulae, within small experimental errors. Similarly, the relation of dispersion to the width of the D lines in absorption, measured visually, is found to agree with that predicted classically. By these purely optical methods a value of the *"radius" of the electron* can be found. It is in order of magnitude 10^{-13} cm. Further study, employing a densitometer, will be necessary to determine an exact value.

Experimental Results

A MICHELSON interferometer with a 55 cm path in each arm was constructed, and some 600 measurements made by methods previously described.[1] Micrometer measurements were made visually on the width of

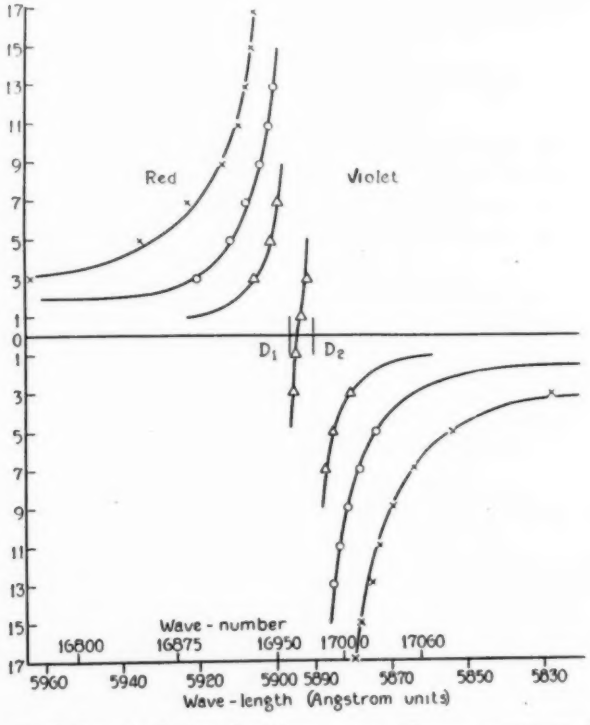

Fig. 1. Refractive index of sodium vapor. Crosses correspond to width of D_1 of 1.5A; circles, 1.0A; triangles, 0.6A.

[1] J. Q. Stewart and S. A. Korff, Phys. Rev. **32**, 676 (1928).

D_1 in absorption, and of the position of the centers of the dark fringes seen at the same time in the spectroscope.

Illustrative resultant values of the phase shift are given in Fig. 1. The crosses, circles, and triangles show the observed phase shifts at three vapor densities, corresponding to three line widths; and the curves give the theoretical values. The curves were drawn for observed line widths of D_1 of 1.5, 1.0 and 0.6 Angstroms respectively. Only one curve is shown between the D lines, corresponding to the line width of 0.6 Angstroms. The three line widths mentioned correspond to 9.9, 3.7 and 1.3×10^{14}, respectively, molecules per sq. cm (as computed from Eq. (2) of the previous paper). The column of vapor was about 10 cm long.

The ordinates of Fig. 1 are in phase shifts in half wave-lengths, and the abscissas in wave-numbers and wave-lengths. The relation of phase shifts to the refractive index is

$$\zeta=2(\mu-1)z/\lambda \tag{1}$$

where ζ is the observed fringe number, (phase shift), λ is the wave-length and z is the length of the column of vapor. Dark fringes were observed, corresponding to odd integral values of ζ.

Fringes were observed and measured between the D lines. It was found, however, that at high vapor densities they became so numerous and closely packed as to be indistinguishable. In the space between the D lines, there are as many fringes as there are on both sides, outside the lines; for at each line the refractive index less unity changes sign. Hence while there are only a few fringes altogether (i.e., at low vapor densities), the fringes between the lines are easy to observe; but at high vapor densities they are too closely packed to be observable. The fringes between the lines ran together, as the vapor pressure was increased, at a point very nearly 2/3 of the distance from D_2 to D_1. This is what would be expected on the hypothesis that there are twice as many atoms active in producing D_2 as D_1.

Theoretical Discussion

The theoretical equation for fringe position previously derived[1] may be written as

$$\zeta\beta_1\beta_2/(\beta_2+2\beta_1)=kw_1^2/8\pi^2a\lambda=B \tag{2}$$

where k is the "contrast factor" at the observed "edge" of the line, w_1 is the observed width of D_1, a is the "radius of the electron," β_1 and β_2 are the separations of the fringes from D_1 and D_2, respectively, in wave-length. The convention employed takes β positive on the red side, and positive ζ's represent phase "lag." If w_2^2 were employed in (2) in place of w_1^2, the numerical constant would be changed to $16\pi^2$, assuming that twice as many atoms are concerned in D_2 as in D_1.

The experimental method used gives directly values of ζ and β_1 and β_2. But $\beta_2=\beta_1-d$, where d is the ratio of the distance in Angstroms between the

D lines to the wave-length 5890 Angstroms. We can thus eliminate β_2. Define P (a pure number) as

$$P=\frac{3\beta_1-d}{\beta_1(\beta_1-d)}. \tag{3}$$

Then (2) reduces to $\zeta/P=B$.

A graph of P against β_1 and β_2 was plotted on a large scale. Then for each of the 600 measurements of β_1 and β_2 a value of P was read from the curve. The 600 were then separated into 16 groups, according to the width of w_1 that each corresponded to, ranging from 1.9 to 0.25 Angstroms. In each group, the temperature of the vapor was constant while the line width and fringe positions were measured. The wider lines correspond of course to the higher temperatures. The temperatures ranged from about 180°C to 320°. The values of P thus obtained were divided into the observed ζ for each, and a value of B obtained. Thus for each observed width of D_1 in absorption a set of values for B is obtained. Now the average value of B for each width divided into the width squared should equal a constant, as C, where

$$C=w_1^2/B=8\pi^2 a\lambda/k \tag{4}$$

The constant C given by these 16 sets was 208 ± 16.9. Thus the constancy expected held with a probable error of 8 percent. The variations can be ascribed to experimental error.

Dividing the averaged constant C by the average B for each case, thirty-two calculated widths, w_1, were obtained. The mean discrepancy regardless of sign, of these with the corresponding observed values was 0.03 Angstroms. This is a remarkably good agreement considering the approximate method of measuring line width. Accordingly the idea is confirmed that line width can be computed directly from refractivity.

From the average C and calculated w_1, a calculated value of B was obtained for each case, and from these, dividing into a set of ζ's, a set of calculated β's was obtained for each case, which were plotted as theoretical curves, as in Fig. 1. The agreement with the observed values of the fringe position can be seen by inspection. The curves in Fig. 1 are representative.

An example will clarify the discussion.

Observed				P from graph		$B=\zeta/P$	
w_1	ζ	β red	β vio	red	vio	red	vio
0.6A	3	9	16	1600	1600	0.0019	0.0019
0.6	5	4	11	2600	2750	0.0019	0.0018
0.6	7	2.5	9.7	3700	3900	0.0019	0.0018

From the relation $C=w_1^2/B$, we get a calculated C of 195 (Angstroms)^2, which is near the mean C of all observations. Now if we reverse the calculations, employing the mean C, 208, we get a calculated value of $w_1=0.62$. Calculating B for this value, we find it to be 0.0019, and from $B=\zeta/P$, we get a value of P for each ζ. Now from the graph of P and β_1, we read off the values of β_1 which are found to be

β_1 (red)	9	4	3
β_1 (violet)	16	11	9

These will be seen to agree well with the observed values. This example is typical.

The exact identification of the fringe number ζ gave trouble, for the first dark fringe, $\zeta = 1$, was always broad and diffuse and hard to see. The question was finally settled by using a spectroscope of much lower resolving power, in which the first fringe could be seen. The difficulty of assigning the correct ζ to a given fringe is a weakness in this method of measurement of refractivity.

The Contrast Factor

Substituting in (4), the average value of the constant C, together with $a = 1.88 \times 10^{-5}$ Angstroms, and $\lambda = 5890$ Angstroms, the value of k is found to be 0.04.

This corresponds to the ratio at the observed edge of the line between light at the edge and light in the continuous background of 0.96, which is surprisingly high. Still it is unnecessary to suppose that a differs in order of magnitude from the assigned value. All the lines would have been seen correspondingly narrower with lower visual sensitivity, but the forms of the relations would not be affected.

Measurements of the lines with a densitometer are required before definite conclusions can be drawn as to the "radius" of the electron. It may be that a, as calculated from (4) when an objectively determined k is available will differ somewhat from the value assumed above.

Remarks

The work shows that, as regards the variation in refractivity and the opacity, corresponding to the D lines, sodium atoms behave as classical oscillators, within the limits of the experimental error, i.e., to about 8 percent.

This is in agreement with the results of Roschdestwensky[2] and those of Ladenburg and Kopfermann,[3] whose quantum dispersion formula can readily be reduced to the one used herein. The experimental method used differs from theirs, and they did not study they relations between refractivity and and line-width. It is indicated that the "absorption" in the D lines is primarily scattering of the Rayleigh-Lorentz type, at least near their edges.

It is planned to investigate the effects of the presence of inert gases on the refractive index. In a preliminary test, the introduction of several centimeters of argon did not much affect the fringes formed by the sodium.

The question arose whether the fringes would be more sensitive than the lines themselves to Zeeman effect. It can readily be shown that if the wavelengths of the components of a line are separated by a magnetic field by λs, the phase shift will be

[2] Roschdestwentsky, Ann. d. Physik **39**, 307 (1912).
[3] Ladenburg und Kopfermann Zeits. f. Physik **48**, 15 (1928).

$$\zeta = 2B \cdot \frac{\beta_1+\beta_2}{\beta_2\beta_1} \tag{5}$$

where the components are assumed of equal intensity.
Writing $\beta_2=\beta_1-s$, and assuming s/β small, this leads to

$$d\zeta/\zeta = -\tfrac{1}{2}ds/\beta \tag{6}$$

where s is varied.

From this it is obvious that the fringes are not specially sensitive. A test showed that a field of 100 gauss was too small to produce any observable effect.

The position of the fringes is not sensitive to the ratio, j, of the number of atoms active for D_2 to that for D_1. In Eq. (2) j was assumed as 2; a more general form is:

$$\frac{\zeta\beta_1\beta_2}{\beta_1+\beta_2} = \frac{kw_1^2}{4j\pi^2 a\lambda} . \tag{7}$$

Curves of P, similar to Eq. (3), were calculated from (7) for various values of j. The observations of β, however, are fitted about equally well over a range of j's. Measurement of line width gives a better discrimination.

I wish to thank Professor J. Q. Stewart for his continuous criticism of this work.

Note: A. S. Fairley[4] in his work on line width in sodium, found that where theory calls for a straight line in the line width to temperature relation, the observed curve departs from this at the bottom, the observed lines appearing too wide. This appears to be due to the insufficient resolving power of the spectroscope for fine lines. By working in higher orders the theoretical relation was found to hold to much narrower line widths. The evidence indicated that the classical line width formula holds for as low vapor pressures as produce observable absorption.

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December 20, 1928.

[4] A. S. Fairley, Astrophys. J. **67**, 114 (1928).

THE DIFFRACTION OF LIGHT BY A CIRCULAR OPENING AND THE LOMMEL WAVE THEORY

By Mason E. Hufford and Harold T. Davis

Abstract

The purpose of this paper is to check the energy in a diffraction pattern of 70 rings secured by passing monochromatc light through a circular orifice. The assumptions made are those of the classical wave theory of light and the mathematical development follows that given in the celebrated papers of E. Lommel. The mathematical interest centers in the discovery of divergent series asymptotic to the Lommel functions $U_1(x)$ and $U_2(x)$.

Photographs of diffraction patterns by circular openings 1.492 cm and 1.832 cm respectively in radius are shown. The smaller of these was used for a comparison of the radii of the diffraction rings calculated by the equations of Lommel's theory with radii measured from the pattern. Graphs of the functions, M^2, J_1, U_2, U_1 are shown. Values of these functions were calculated for 256 values of x where x represents the root values of $J_1(x)=0$ and $J_0(x)=0$. The comparison of measured and calculated radii is shown in a table with the percent of difference. The agreement is also shown by a graph. The striking agreement of the calculated energy with that found in the diffraction pattern, particularly as shown in the broadening and darkening of the rings toward the outer part of the pattern, gives renewed confidence in the classical theory of light as applied to diffraction phenomena.

Introduction

A FEW years ago any problem that had as its aim a checking of the wave theory of diffraction would have been regarded as academic. But the impasse to which the theory of light has been brought by the discovery of the phenomena underlying quantum mechanics has made it again desirable to see how far the interference theory of diffraction, particularly as it has been developed in the classical memoirs of E. Lommel,[1] is in agreement with experiment. With this in mind Professor Hufford secured through a circular orifice the diffraction patterns reproduced in Figures 1 and 2. The large number of rings and the broadening and darkening of the bands toward the outer part of the pattern afforded excellent phenomena to be used in the check of the Lommel theory. Because of the slow convergence of the series expansion of the Lommel functions employed in the calculation of the distribution of energy in the pattern it was found necessary to look for a divergent series which would furnish an asymptotic representation of the functions. This mathematical investigation is contributed by Professor Davis.

Because of the long range over which the energy distribution was calculated existing tables for the roots of the Bessel functions $J_0(x)$ and $J_1(x)$ with the corresponding values of $J_1(x)$ and $J_0(x)$ were extended from

[1] E. Lommel, Abh. der K. Bayer. Akad. der Wissen. **15**, 233–531 (1884–1886).

40 roots to 150 in the one case and from 50 roots to 150 in the second.[2] A contribution from the funds of the Waterman Institute of Indiana University made these calculations possible. Two independent computations of the energy were made and the work was further checked by an independent calculation of the square of the intensity at the root values of $U_2(x)$ which were positions of maximum or minimum energy.[3]

The particularly noteworthy feature of this investigation is the close agreement of experiment and theory. The rings, as is obvious from the energy diagram, Figure 3, (A), broaden and become darker toward the outer part of the plate.

Computation of the Energy [4]

If a monochromatic beam of light of wave-length λ and period T propagated in spherical waves from a point source A, is allowed to pass through a small circular orifice of radius r, it can be shown that the intensity of illumination at a point P on a screen perpendicular to the axis of the beam is proportional to the square root of

$$I^2=\frac{1}{a^2b^2\lambda^2}(C^2+S^2),$$

in which we abbreviate,

$$C=\int_0^{2\pi}\int_0^{r}\cos\frac{2\pi}{\lambda}\{(a+b)\rho^2/2ab-\zeta\rho\cos\phi/b\}\rho\,d\rho\,d\theta,$$

$$S=\int_0^{2\pi}\int_0^{r}\sin\frac{2\pi}{\lambda}\{(a+b)\rho^2/2ab-\zeta\rho\cos\phi/b\}\rho\,d\rho\,d\theta,$$

where a is the distance of A from the edge of the orifice, b the distance of the screen from the nearest point or pole of the spherical wave, and ζ, the distance of P from the axis of symmetry. The only assumption made in this formula is that the radius is sufficiently small and P sufficiently near the axis so that we may use b for the distance from any element of the wave front in the orifice to P.

Our point of departure is from the square of Lommel's expression for the intensity of illumination at a point x from the axis of symmetry, which is proportional to

$$M^2=U_1^2+U_2^2, \tag{1}$$

in which we abbreviate,

$$U_1(x)=\sin\tfrac{1}{2}y^2(1+\omega^2)-V_1(x), \tag{2}$$

$$U_2(x)=-\cos\tfrac{1}{2}y^2(1+\omega^2)+V_0(x), \tag{3}$$

[2] A new Table of the Zeros of the Bessel Functions, H. T. Davis and W. J. Kirkham, Bull. Amer. Math. Soc. **33**, pp. 760–772 (1927).

[3] This computation was greatly assisted by W. J. Kirkham and V. V. Latshaw.

[4] See Gray, Mathews and MacRobert, Bessel Functions, MacMillan (1922), Chapter XIV.

$$V_0(x)=J_0(x)-\omega^2J_2(x)+\omega^4J_4(x)-\cdots \tag{4}$$

$$V_1(x)=\omega J_1(x)-\omega^3J_3(x)+\omega^5J_5(x)-\cdots \tag{5}$$

where $\omega=x/y$, $y=4\pi r^2(a+b)/2\lambda ab$ and $J_n(x)$ is the Bessel function of first kind of order n. The series defining V_0 and V_1 are clearly convergent since $\lim_{n=\infty}J(x)_{n+2}/J(x)_n=\lim_{n=\infty}\ x^2/4(n+1)(n+2)=0$, but the convergence for comparatively large values of x becomes exceedingly slow and tables of $J_n(x)$ are not available beyond $x=24$ when $n>1$.

In view of the fact that we have

$$\frac{\partial M^2}{\partial x}=-2\left(\frac{2}{y}\right)^2J_1(x)U_2(x),$$

from which it appears that maximum and minimum values of the energy occur at the roots of $J_1(x)=0$ and $U_2(x)=0$, it is clearly desirable to evaluate $V_0(x)$ and $V_1(x)$ at the root values of the first equation, which we designate by $x_1^{(S)}$, where S is the number of the root. Since it is also desirable to interpolate values at stations between $x_1^{(S+1)}$, and $x_1^{(S)}$, we shall also compute $V_0(x)$ and $V_1(x)$ at the zeros of $J_0(x)$, designating these values by x_0. It thus becomes convenient to express $V_0(x)$ and $V_1(x)$ in terms of $J_0(x)$ and $J_1(x)$. This is accomplished by means of the series:[2]

$$\begin{aligned}J_{2n}(x)=(-1)^n&\left[1+\sum_{r=1}^{n-1}(-1)^r\frac{2^{2r}n^2(n^2-1)^2\cdots[n^2-(r-1)^2]^2(n^2-r^2)}{(2r)!\ x^{2r}}\right]J_0(x\\&+(-1)^{n+1}\left[\sum_{r=0}^{n-1}(-1)^r\frac{2^{2r+1}n^2(n^2-1)^2(n^2-4)^2\cdots(n^2-r^2)^2}{(2r+1)!\ x^{2r+1}}\right]J_1(x).\end{aligned} \tag{6}$$

$$\begin{aligned}J_{2n-1}(x)=(-1)^{n+1}&\left[\sum_{r=0}^{n-2}(-1)^r\frac{2^{2r+1}n^2(n^2-1)^2\cdots[n^2-(r-1)^2]^2(n^2-r^2)(n-r)(n-r-1)}{(2r+1)!\ x^{2r+1}}\right]J_0(x)\\&+(-1)^{n+1}\left[1+\sum_{r=1}^{n-1}(-1)^r\frac{2^{2r}n^2(n^2-1)^2\cdots[n^2-(r-1)^2]^2(n-r)^2}{(2r)!\ x^{2r}}\right]J_1(x)\end{aligned} \tag{7}$$

Substituting (6) in (4) and (7) in (5) we get,

$$\begin{aligned}V_0(x)&=\sum_{n=0}^{\infty}(-1)^n\omega^{2n}J_{2n}(x),\\&=\sum_{n=0}^{\infty}\omega^{2n}[1-2^2n^2(n^2-1)/2!x^2+2^4n^2(n^2-1)^2(n^2-4)/4!x^4-\cdots]J_0(x)\\&\quad-\sum_{n=0}^{\infty}\omega^{2n}[2n^2/x-2^3n^2(n^2-1)^2/3!x^3+2^5n^2(n^2-1)^2(n^2-4)^2/5!x^5-\cdots]J_1(x)\end{aligned} \tag{8}$$

$$\begin{aligned}V_1(x)&=\sum_{n=1}^{\infty}(-1)^{n+1}\omega^{2n-1}J_{2n-1}(x),\\&=\sum_{n=1}^{\infty}\omega^{2n-1}[2n(n-1)/x-2^3n^2(n^2-1)(n-1)(n-2)/3!x^3\\&\qquad+2^5n^2(n^2-1)^2(n^2-4)(n-2)(n-3)/5!x^5\cdot-\cdots]J_0(x)\\&\quad+\sum_{n=1}^{\infty}\omega^{2nr}[1-2^2n^2(n-1)^2/2!x^2+2^4n^2(n^2-1)^2(n-2)^2/4!x^4-\cdots]J_1(x).\end{aligned} \tag{9}$$

Defining a new function,

$$S_m(x) = \sum_{n=1}^{\infty} n^m x^n,$$

we see that $S_m(x)$ can be evaluated for any subscript from the relations:

$$S_0(x) = x/(1-x), \quad S_{m+1}(x) = x\frac{d}{dx}S_m(x).$$

Making use of the formulas thus obtained we can evaluate the sums in (8) and (9). For example,

$$\sum_{n=0}^{\infty} \omega^{2n} n^2(n^2-1) = S_4(\omega^2) - S_2(\omega^2) = 12(\omega^4+\omega^6)/(1-\omega^2)^5.$$

We thus derive the following asymptotic series:

$$V_0(x) \sim \left\{ \frac{1}{1-\omega^2} - \frac{24\omega^4(1+\omega^2)}{x^2(1-\omega^2)^5} + \frac{1920\omega^6(1+6\omega^2+6\omega^4+\omega^6)}{x^4(1-\omega^2)^9} - \cdots \right\} J_0(x)$$
$$- \left\{ \frac{2\omega^2(1+\omega^2)}{x(1-\omega^2)^3} - \frac{48\omega^4(1+9\omega^2+9\omega^4+\omega^6)}{x^3(1-\omega^2)^7} \right.$$
$$\left. + \frac{3840(1+25\omega^2+100\omega^4+100\omega^6+25\omega^8+\omega^{10})}{x^5(1-\omega^2)^{11}} - \cdots \right\} J_1(x)$$

$$V_1(x) \sim \left\{ \frac{4\omega^3}{x(1-\omega^2)^3} - \frac{192\omega^5(1+3\omega^2+\omega^4)}{x^3(1-\omega^2)^7} \right.$$
$$\left. + \frac{23040\omega^7(1+10\omega^2+20\omega^4+10\omega^6+\omega^8)}{x^5(1-\omega^2)^{11}} - \cdots \right\} J_0(x)$$
$$+ \left\{ \frac{\omega}{1-\omega^2} - \frac{8\omega^3(1+4\omega^2+\omega^4)}{x^2(1-\omega^2)^5} \right.$$
$$\left. + \frac{384\omega^5(1+16\omega^2+36\omega^4+16\omega^6+\omega^8)}{x^4(1-\omega^2)^9} - \cdots \right\} J_1(x).$$

It is beyond the scope of this paper to discuss the asymptotic character of these series. They are unusual, however, in the range to which they apply. For small values of x their convergence is accelerated by the smallness of ω^2 and for small values of $1-\omega^2$ convergence is secured through large values of x. In the calculations of the present paper, $y = 443.87$ and the range of x is from 0 to 400. For $x = 24$, $\omega^2 = 0.0029$ the series converges to $V_0(x)$ with an error not greater than 42×10^{-10}. For $x = 393.48$ and $\omega^2 = 0.7859$ the error does not exceed 0.006 which is well within the error of the experiment.

In checking the energy diagram the values of M^2 were also calculated at each of the 57 roots of $U_2(x) = 0$. These roots and the corresponding values of $V_0(x)$ and $V_1(x)$ were calculated by interpolation.

Experimental

In a previous paper[5] some experiments were described in which diffraction patterns were produced by light diffracted about spherical objects. The theory of Lommel for this type of diffraction was verified for the range presented by the experiment. The diffraction patterns shown in this paper are those in which monochromatic light passed through circular openings. These patterns are unusually large for this type of diffraction and offer therefore an opportunity to verify the Lommel theory for this case through a wider range than has been possible before. In Lommel's original paper is contained a description of a check of theory by experiment in which he produced a system of five microscopic rings through a needle hole in paper.

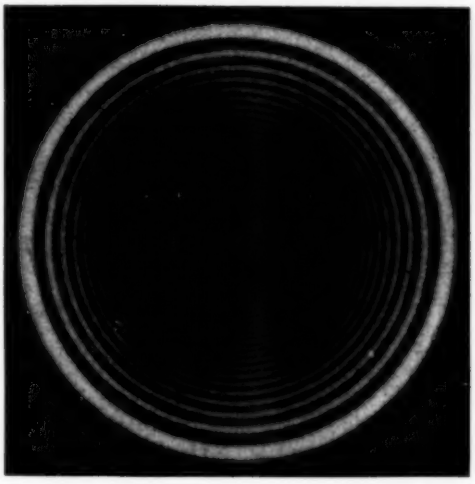


Fig. 1. Diffraction pattern, opening 1.492 cm.

The agreement through that short range was very satisfactory. Figure 1 of the patterns here shown was selected for the purpose of verification and Figure 2 is included because of the large number of diffraction rings which it contains.

For the purpose of producing these diffraction patterns apparatus similar to that described in a previous paper[6] was arranged. Figure 1 was obtained by light through an opening 1.492 cm in radius and Figure 2 by an opening 3.664 cm in radius. These openings made in lead plates were mounted at a distance $a = 1552$ cm from a light source 0.022 cm in diameter. The distance from the diffracting object to the receiving screen was $b = 1706$ cm. The edges of the openings were polished smooth. Monochromatic light of wave-length 3880A was isolated from the carbon spectrum and passed through the hole at the source. The exposure was for three hours. By the conditions of the experiment, the value of y in the Lommel equations becomes $y = 443.87$.

[5] Hufford, Phys. Rev. **7**, 545 (1916).
[6] Hufford, Phys. Rev. **3**, 241 (1914).

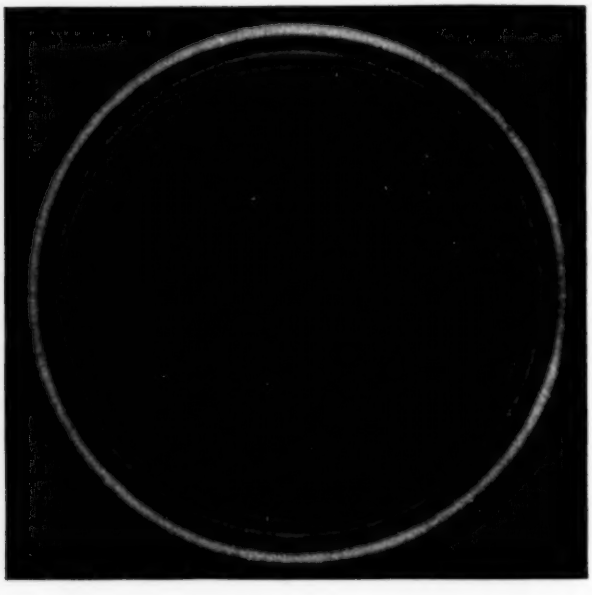


Fig. 2. Diffraction pattern, opening 3.664 cm.

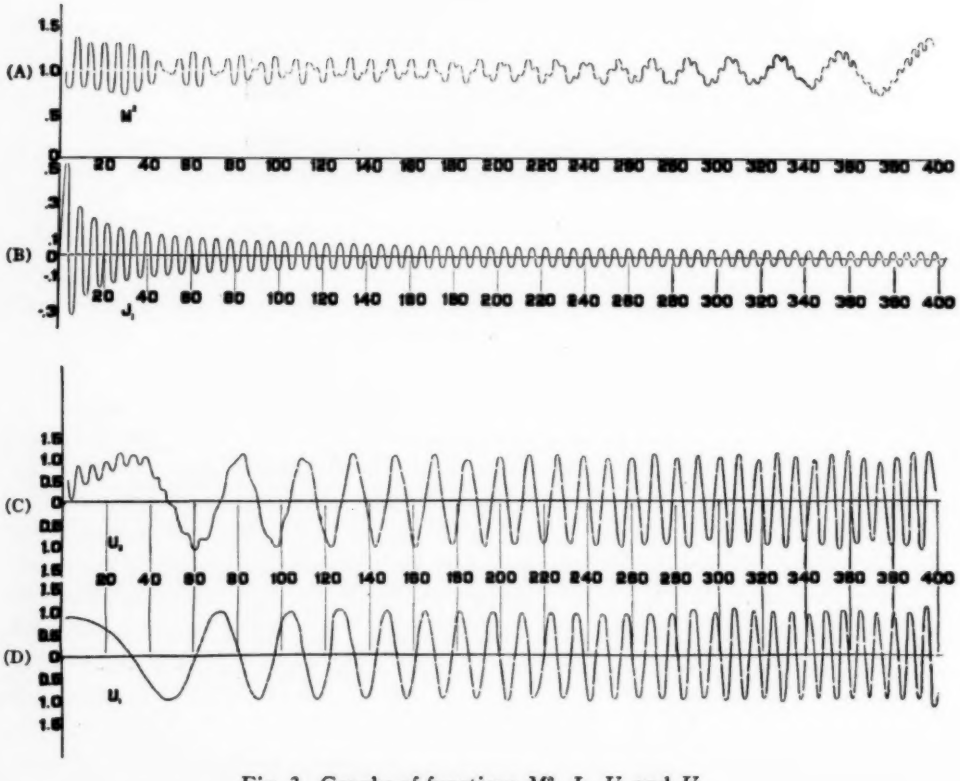


Fig. 3. Graphs of functions M^2, J_1, U_2 and U_1.

The values of $U_1(x)$ and $U_2(x)$ for this pattern have been calculated using values of x corresponding to the roots of $J_1(x)=0$ and $J_0(x)=0$, by the use of the asymptotic series $V_0(x)$ and $V_1(x)$ substituted in equations (2) and (3). Each of the calculations involved in obtaining values for the terms of the coefficients of $J_0(x)$ and $J_1(x)$ were made separately by each of us and results were checked. The graphs $U_1(x)$ and $U_2(x)$ were plotted throughout the range of the pattern of Figure 1 at the values of x corresponding to the roots of $J_0(x)=0$ and $J_1(x)=0$. These graphs are shown in Fig. 3 *C* and *D*. It is the sum of the squares of the ordinates of these graphs which give M^2 proportional to the energy. The value of M^2 plotted as ordinates at the same values of x as used in the graphs mentioned gives the energy curve. This curve is shown in Fig. 3 *A*. From this graph of intensity, maxima and minima of light energy in the diffraction pattern are clearly

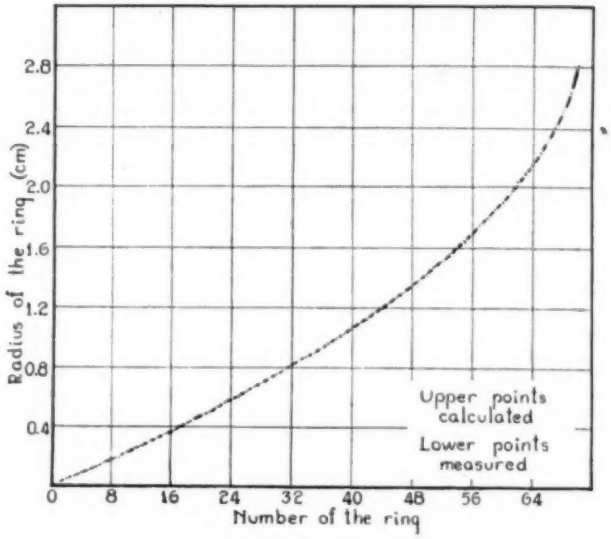


Fig. 4. Graphical comparison of the theoretical and experimental values of the radii of the diffraction rings.

indicated. It will be observed that secondary maxima and minima are shown. It was impossible to detect these on the photographic plate due to the failure of the plate in showing such small differences in intensity.

Since the roots of $J_1(x)=0$ as well as those of $U_2(x)=0$ are critical values for maxima and minima, the graph of $J_1(x)$ is also shown in Fig. 3 *B*.

In order to compare theory with experiment, the values of x for maxima and minima were read from the graph of M^2. These were substituted in Lommel's equation, $\zeta = b\lambda x/2\pi r$ where ζ is the radius of the bright or dark diffraction ring and r is the radius of the diffracting opening. The radii of the bright and dark rings of the pattern in Fig. 1 were measured by micrometer microscope from the photographic plate. Table I includes the averages of ten independent measurements of the rings and the radii as computed from Lommel's equation. The percent of difference is also given.

The agreement is also represented graphically in Fig. 4. It will be observed in the energy diagram, Fig. 3 *A*, that at the fifteenth ring and again at the twenty first, there is a change in the intensity as compared to the adjacent dark rings. It was hoped that sufficient refinement could be developed in the experiment to show this difference. However all the diffraction photographs fail to show the effect, to any degree of certainty. The failure is probably accounted for by the small difference in intensity between these rings and the dark rings on either side. At no place do the dark rings represent a total absence of light. The graph Fig. 3 *A* shows that the dark rings have approximately two thirds the intensity of the bright rings. However in the outer rings the difference becomes greater as the theory predicts and experiment confirms. From the graph Fig. 3 *A*, the fifteenth and twenty first rings are approximately eighty five percent as intense as the adjacent bright rings and only about twenty percent brighter than the dark rings of the region. The photographic plates used did not show this small difference.

TABLE I. *Observed and calculated radii of diffraction rings* $y=443.87$; $r=1.492$ *cm.*

No.	Intensity	χ for $J_1(\chi)=0$ or $U_2(\chi)=0$	Radius (calc.)	Radius (obs.)	Per cent diff.	No.	Intensity	χ for $J_1(\chi)=0$ or $U_2(\chi)=0$	Radius (calc.)	Radius (obs.)	Per cent diff.
1	D	J	0.0271	0.0294	8.0	36	B	J	0.9372	0.9345	0.3
2	B	J	0.0495	0.0482	3.0	37	D	U	0.9594	0.9685	1.0
3	D	J	0.0718	0.0740	3.0	38	B	J	1.0047	0.9986	0.6
4	B	J	0.0941	0.0938	0.3	39	D	J	1.0259	1.0323	0.6
5	D	J	0.1163	0.1189	2.0	40	B	J	1.0703	1.0624	0.7
6	B	J	0.1385	0.1399	0.3	41	D	J	1.0924	1.0988	0.6
7	D	J	0.1607	0.1653	3.0	42	B	J	1.1368	1.1313	0.5
8	B	J	0.1829	0.1852	1.0	43	D	U	1.1692	1.1676	0.1
9	D	J	0.2051	0.2103	2.0	44	B	J	1.2033	1.2029	0.0
10	B	J	0.2273	0.2303	1.0	45	D	J	1.2255	1.2399	1.0
11	D	J	0.2495	0.2549	2.0	46	B	U	1.2815	1.2763	0.5
12	B	J	0.2717	0.2758	2.0	47	D	J	1.3143	1.3160	0.1
13	D	J	0.2939	0.3005	2.0	48	B	J	1.3586	1.3505	0.6
14	B	J	0.3160	0.3223	2.0	49	D	U	1.3909	1.3939	0.2
15	D	U	0.3361	0.3495	4.0	50	B	U	1.4368	1.4319	0.4
16	B	J	0.3604	0.3759	4.0	51	D	U	1.4849	1.4754	0.6
17	D	J	0.4048	0.4047	0.0	52	B	J	1.5139	1.5137	0.0
18	B	J	0.4270	0.4284	3.0	53	D	J	1.5583	1.5602	0.1
19	D	J	0.4491	0.4532	0.9	54	B	J	1.6026	1.6029	0.1
20	B	J	0.4713	0.4761	1.0	55	D	J	1.6470	1.6511	0.3
21	D	J	0.4935	0.5023	2.0	56	B	U	1.7034	1.6973	0.4
22	B	J	0.5379	0.5303	1.0	57	D	J	1.7580	1.7498	0.5
23	D	J	0.5601	0.5610	0.2	58	B	J	1.8023	1.7962	0.3
24	B	J	0.5823	0.5851	0.5	59	D	U	1.8591	1.8543	0.3
25	D	J	0.6040	0.6127	1.0	60	B	J	1.9132	1.9039	0.5
26	B	J	0.6488	0.6392	2.0	61	D	U	1.9683	1.9646	0.2
27	D	J	0.6710	0.6689	0.3	62	B	U	2.0370	2.0239	0.6
28	B	J	0.6932	0.6963	0.5	63	D	U	2.1034	2.0945	0.4
29	D	U	0.7350	0.7251	1.0	64	B	U	2.1671	2.1576	0.4
30	B	J	0.7597	0.7531	1.0	65	D	U	2.2326	2.2387	0.3
31	D	J	0.7819	0.7843	0.3	66	B	U	2.3244	2.3151	0.4
32	B	U	0.8198	0.8119	1.0	67	D	U	2.4120	2.4073	0.2
33	D	J	0.8485	0.8437	0.4	68	B	U	2.5249	2.5121	0.5
34	B	J	0.8706	0.8732	0.3	69	D	J	2.6452	2.6365	0.3
35	D	U	0.9010	0.9060	0.5	70	B	J	2.8005	2.8317	1.0

As shown in the intensity graph, Fig. 3 *A*, the theory indicates that there is a system of fine fringes superimposed upon the dark and bright rings. These the photographs also fail to show. In accounting for this failure along with that pointed out above it should be mentioned that with a source 0.022 cm in diameter and approximately equal distances from plate and opening on the one side and source and opening on the other, the dark rings should have an increased width equal to the diameter of the source. This would tend to obliterate details as minute as these fringes.

It should be mentioned also that with a source as large as that used here, the light cannot be regarded as strictly monochromatic. This also would tend to smooth out the intensity in the dark rings and obscure the superposed fringes.

Despite the want of these details in the photographs the fact that they verify the theory in respect to the number of rings and their radii and that the rings become more intense and more widely separated in the outer regions is a triumph for the theory presented by Lommel. The photographs are of interest also because of the great number of rings and the large diffraction patterns produced through large distances.

Conclusion

The diffraction photographs here shown are large patterns for this type of diffraction. The very large number of rings has offered an opportunity for testing the classical wave theory as developed by Lommel for this range. This is of special interest as a wider application of the wave nature of light at a time when the assumption has been challenged by experiments underlying the quantum theory of radiant energy. The agreement obtained between theory and experiment lends new confidence to the wave theory.

Waterman Institute for Research,
Indiana University,
August, 1928.

DEPENDENCE OF ELECTRON EMISSION FROM METALS UPON FIELD STRENGTHS AND TEMPERATURES

By Robert A. Millikan and Charles C. Lauritsen

Abstract

This paper contains a full presentation of the reasons for believing, contrary to results recently obtained elsewhere, that field currents are only independent of temperature up to about 1100°K, and that at that temperature the energy of thermal agitation begins to assist the fields appreciably in causing the escape of electrons from metals. The precise form of function describing this dependence is not accurately determinable experimentally, but the form originally suggested by us fits the facts of observation thus far known satisfactorily, not better, however, than does the theoretical form suggested by Houston.

WHEN we first published the now well established experimental field-current equation

$$i=Ce^{-b/F} \tag{1}$$

we thought it of interest to combine this with an equation of the usual thermionic form, namely

$$i=Ae^{-b/T} \tag{2}$$

for the sake of attempting to describe what happens in field-current work *at each emitting point* under the joint influence of both field and temperature.

For the sake, however, of obtaining as general an expression as we could then suggest, and at the same time following the most approved thermionic form, we wrote the joint, purely empirical, equation as follows:

$$i=A(T+cF)^2e^{-b/(T+cF)} \tag{3}$$

but in the first place we were careful to state that "the constant c of course changes with the condition of the surface," and also that we had "not yet taken sufficient data to know whether, with a given surface, one value of c will correspond to all values of T."[1]

In the second place we had experimentally tested (3) very fully and carefully for the extreme case in which T is very small in comparison with F, i.e., for the case of fields so powerful that (3) reduces to (1), and hence b becomes independent of F, but we had taken only meagre experimental data for the region in which the effect of T begins to be comparable with that of F; so that just how b varied with F for weak fields was unknown to us, though the fact that it was presumably some function of F and T had been discussed at length in the earlier paper by Millikan and Eyring.[2] *In*

[1] Millikan and Lauritsen, Proc. Nat. Acad. Sci. **14**, 15 (1928).

[2] Millikan and Eyring, Phys. Rev. **27**, 51 (1926).

other words, we had from the first regarded both b and c as some sort of functions of F and T, and as a matter of fact at the time of the publication of equation (3) we were initiating new experiments to find something more about the nature of these two functions.

We had, however, made sufficient experiments long before the date of publication of equations (1) and (3) to convince ourselves of the correctness of the qualitative conclusion drawn first by Millikan and Eyring[2] and later stated by us in equation (3) that while field-currents are practically independent of temperature below say 1000°K, *they begin to become definitely dependent upon temperature in the case of tungsten at about 1100°K*. This conclusion is questioned by de Bruyne[3] on new experimental grounds.[4] Also Fowler and Nordheim[5] while deducing (1), following Oppenheimer,[6] from the wave-mechanics, "fail to find any theoretical justification for (3)," though they say that "of course some justification may exist."

This is sufficient to show how important it is to determine if possible, *first*, just how "*b*" depends upon the field *F* before, with rising *F*, it has lost such dependence and equation (1) has taken control of the situation, and, *second*, whether field currents can be definitely shown to depend on *T*.

The first question we cannot yet answer fully, but we can throw some light upon it. It seemed to be partially answered by Millikan and Eyring's proof that the Schottky theory is not applicable to field currents. This theory assumes that the externally applied field simply acts to neutralize partially the work function *b*, and so long as these fields are not too strong the Schottky theory demands a linear relation between log *i* and $F^{1/2}$, a relation unambiguously shown by Millikan and Eyring's paper not to hold in *field-current* phenomena. Recently, however, Phorte[7] and de Bruyne[4] have beautifully verified this equation in the case of *ordinary thermionic* discharge, as Schottky himself had earlier done, the range over which *F* is varied in de Bruyne's experiments being larger than had been used before, *but still very small in comparison with the actual fields used in field current experiments* (see below).

We wish to point out, however, that contrary to de Bruyne's belief there is no discrepancy at all between his results, Millikan and Eyring's, or our own. The reason that the Schottky equation holds for ordinary thermionic emission but not for field emission is as follows: Field emission, as Millikan and Eyring[2] long ago pointed out only takes place from one or two minute spots—"microscopic mountain peaks"—where the applied potential gradient is a hundred times greater than that computed from the applied potential and the radius of the wire, in other words where the field strength is *enormously* high—so high that no image law, such as underlies Schottky's theory—can possibly apply. On the other hand, in *ordinary*

[3] N. A. de Bruyne, Proc. Cambridge Phil. Soc. **24**, part 4, 518 (1928).
[4] N. A. de Bruyne, Proc. Roy. Soc. **A120**, 423 (1928).
[5] Fowler and Nordheim, Proc. Roy. Soc. **A119**, 173 (1928).
[6] Oppenheimer, Phys. Rev. **31**, 66 (1928).
[7] W. L. Phorte, Zeits. f. Physik **49**, 46 (1928).

thermionic emission, since the electrons are here being boiled out from the *whole surface* of the wire, the applied external field is on the average just that computed from the applied potential and the wire-radius, and is therefore very small (Millikan and Eyring estimated it of the order of one two-hundredths of that existing at a point which is a source of field currents) and hence must follow the image law. *In other words, the image law, and hence the Schottky equation, should hold for the relatively weak fields existing at the smooth surface of a wire, but it is definitely shown by the Millikan-Eyring field-current work not to hold for the very strong fields existing at the emitting points in field-current phenomena, and the validity of (1) proves that for strong enough fields b has become quite independent of F.*

This, then, is the answer as far as it can now be given to the first of the foregoing questions. *For weak enough fields b is to be diminished by a quantity which is proportional to $F^{1/2}$ but for strong fields becomes independent of F.*

As for the second question, the quantitative evidence is still very strong that the rise in field-currents observed by Millikan and Eyring at 1100°K is a real effect of temperature upon *the field currents themselves* and not the mere influence of the field in augmenting, in accordance with the Schottky equation, the thermionic current begining to set in at 1100°K. This last interpretation, given by de Bruyne, we think to be incorrect for the following reasons.

First, the thermionic currents setting in at 1100° K from the tungsten wire used in Millikan and Eyring's experiment amount, even when augmented by the Schottky effect due to the highest field employed, to a current of but 10^{-12} amperes, whereas the observed currents at the highest field (see Table VII, Phys. Rev. *27*, 61 1926) amounted to 10^{-4} amperes. This means that the observed *increase* in these field currents (of strength 10^{-4} amperes) of from 10 percent to 20 percent brought about by increasing the temperature from 300°K to 1100°K is not at all the Schottky or field increase in the thermionic currents. It is about a billion times too large to be so interpreted. It must be rather a real temperature effect on the field current itself that begins to set in appreciably at about 1100°K. The interpretation given by deBruyne which makes field currents from tungsten independent of temperature up to about 1900°K is completely irreconcilable with the Millikan and Eyring experimental data given in Table VII of their paper.

Second, the foregoing results have been checked many times in the work herewith presented and with many different wires of different diameters. An altogether typical set of readings on one of these wires is plotted in Fig. 1. The applied potential was here constantly 8000 volts. The wire, of about 0.6 mils diameter, was in the middle of a cylinder of 1.6 cm diameter. The logarithms of the currents corresponding to the various temperature are plotted in the figure. It will be seen that up to 800°K there was no apparent dependence of field currents on temperature: at 800°K the current was 4.6×10^{-8} amperes, while at 1130°K it had risen to 5.6×10^{-8} amperes, an increase of 20 percent due to field alone *at a temperature at which the total thermionic current plus the Schottky effect was not as much as one-thousandth of this*

amount. The figure gives the complete observed curve of the emission of the whole wire as a function of temperature between 700°K and 2500° K at a constant field strength at the surface of the wire, as computed from the radius and the applied potential of 1,440,000 volts. The extreme left side of the curve is, of course, the usual logarithmic straight line representing the ordinary thermionic current from *the whole surface* of the wire, with its slope decreased about 15 percent by the Schottky effect. The right side of the curve gives the *true field currents* from a single point sharp enough so that the field strength at the point is at least 100,000,000 volts, this being the order of magnitude of the field necessary to pull an electron through a surface having a work function of 4.5 volts. The extension downward of the slope on the left shows at once how completely impossible it is to account by means of the Schottky effect for the increase shown on the right in the field currents with temperature.

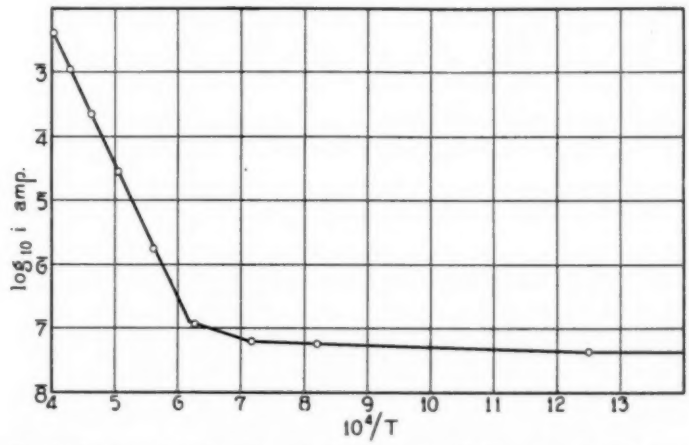


Fig. 1. Typical curve showing the relation between field currents and temperature. Wire #26; 1.56×10^{-3} cm tungsten; $V=8000$ volts.

A third argument is that the Sommerfeld-Houston theory of metallic conduction requires that while at low temperatures there should be, in accordance with the Fermi-Dirac statistics, no appreciable sharing by the electrons of the energy of thermal agitation, as the temperatures increase a condition of equipartition should ultimately be approached. This sharing of thermal energy by the electrons should evidently begin to be appreciable at temperatures at which thermionic emission begins to set in. Dr. Houston[8] has treated this side of the question in a recent theoretical paper, and has found a definite dependence of field emission as such upon temperature.

Wherein then lies the error in de Bruyne's work which leads him to the conclusion that field currents from tungsten are entirely independent of temperature up to 1944°K? His method is to obtain his field currents by subtracting from his observed currents at a given temperature and field-

[8] W. V. Houston, Phys. Rev. **33**, 361 (1929).

strength the computed, or better the extrapolated, thermionic currents as modified by the Schottky effect, and then to plot by means of our equation (1) log i against $1/F$. He thus obtains a series of widely scattering points through which he draws the straight full line shown in Fig. 2, *a line which actually washes out a progression with temperature which appears to us to be shown even by his own data.* For by drawing separate lines through the data taken at each separate temperature, as we have done in our reproduction of de Bruyne's graph in Fig. 2 we think we have shown that his data reveal an increase of field-currents with temperature (see the higher and higher positions of the dotted lines drawn through all the points corresponding to each particular temperature) precisely as do ours and of the same order of magnitude.

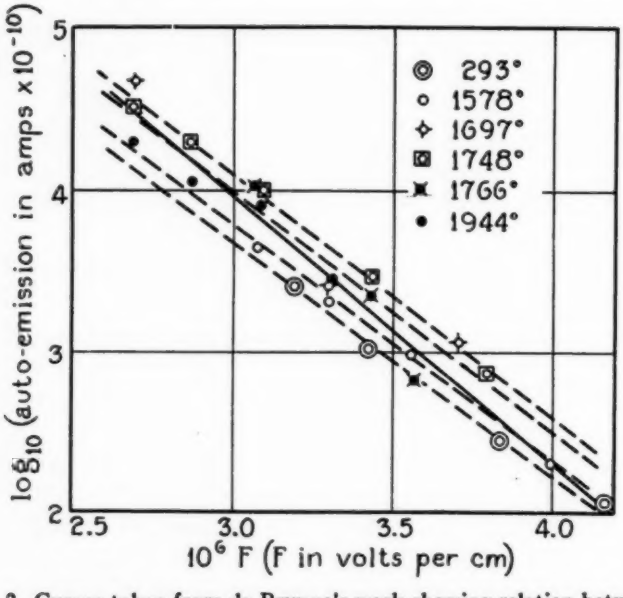


Fig. 2. Curves taken from de Bruyne's work showing relation between field currents and field strength for various temperatures.

But it is after all only his observations taken at the four lowest temperatures that have any significance whatever, for the others are obtained by subtracting from an observed reading a computed or extrapolated reading which differs from the observed by as little as one percent, which is much less than the uncertainty in most field-current measurements. Such observations cannot usually be relied upon to one percent, for the reason that the emitting point does not in general retain its properties unchanged for long periods. Only by keeping fields constant, as was done in the experiments represented in Table VII of reference 2, changing temperatures rapidly, and going back and forth between say 300° and 1100°K, can these fluctuations be avoided. *In a word, we do not think that de Bruyne's work is actually at variance with any of our published conclusions.*

As to the best equational form in which to present the results obtained to date in the domain of field currents de Bruyne suggests the form

$$i = AT^2 e^{-\{\phi-(e^3F)^{1/2}\}/kT} + Ce^{-K/F} \tag{4}$$

The first term is simply the thermionic equation *from the whole surface* as modified by Schottky; the last is our field current equation without indicating its dependence upon temperature. This failure to indicate such dependence we regard as an error, since the last term must, we think, contain T if it is to represent the facts thus far brought to light. Up to the present we have not found a form which is more satisfactory for representing the dependence of field currents upon both F and T than that we originally suggested, namely, $i = A(T+cF)^2 e^{-b/(T+cF)}$, though since we can test this only when temperature is *just beginning* to influence the field current, other forms of dependence upon temperature would doubtless fit the limited experimental data as well. How well this particular form reproduces our own field-current work as well as that of de Bruyne is shown in Fig. 3 in which our own results are plotted as circles, de Bruyne's as crosses[9].

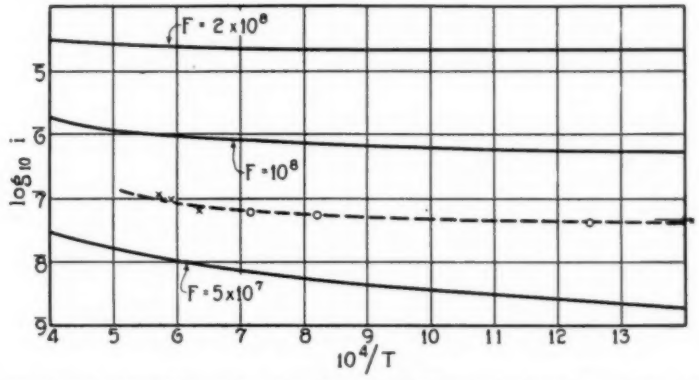


Fig. 3. Curves of variation of $\log_{10} i$ as function of $10^4/T$ as calculated from Eq. (3) for $A = 60$, $b = 52600$, $c = 10^{-4}$, area $= 10^{-14}$. The crosses represent data by de Bruyne.

Equation (3) obviously makes the increase of current with temperature greater for low fields than for high (see Fig. 3), and this result is found to be in agreement with the data in Table VII of reference 2, though the accuracy is perhaps not sufficient to make this experimental conclusion unquestionable.

It must be clearly understood that our equation (3) represents here, and has always been intended to represent, *merely the emission from a particular point under the joint influence, at that point, of field and temperature.* For such a point the Schottky equation cannot be expected to hold, since the image force at such a point has no meaning except for distances that are large compared to the dimensions of the "microscopic mountain peak", i.e., for *very weak* fields.

[9] These points are obtained by taking a vertical section through the dotted lines in Fig. 2 at a suitably chosen value of F.

Our equation (3) makes no attempt to include the thermionic emission from the whole surface of the wire. It is this emission alone to which the Schottky equation applies. This is a phenomenon entirely distinct from field currents and one correctly represented by the first term of de Bruyne's equation (4).

Our equation (3) is merely one way of depicting the fact that energy of agitation begins at some temperature to assist the field in extracting electrons from the point. Dr. Houston has obtained a theoretical expression of this fact which, however, leaves out T from the exponent of (3) but inserts it in the coefficient in much the same way in which it appears in (3). This may be a form more satisfactory than (3), and we shall be glad to use it in preference to (3) if it has better credentials. At present we see no *experimental* way of differentiating between Houston's form and that of (3) since we can only *begin*, as we have done above, to bring to light the effect of temperature in assisting the field electrons to escape. After the thermionic emission from the whole surface sets in it obviously masks the effect of temperature on the point. This thermionic emission from the whole surface, graphically shown by the steep slope on the left of Fig. 1, is something of an entirely different order of magnitude from the effect of temperature on field-currents, represented by the very small slope on the right side of Fig. 1.

NORMAN BRIDGE LABORATORY OF PHYSICS,
CALIFORNIA INSTITUTE, PASADENA,
January 24, 1929.

THE RATE OF FORMATION OF NEGATIVE IONS BY ELECTRON ATTACHMENT

By Austin M. Cravath*

Abstract

By a new method, the fraction h of the collisions between electrons and molecules which result in the attachment of the electron to form a negative ion has been measured in air and oxygen as a function of the average electron energy, the gas pressure, and the moisture content. In oxygen h had a minimum at 0.9 volts average electron energy, and increased with either increase or decrease of the energy from this value. In air h increased as the average electron energy was reduced below 0.9 volts. The absolute value was about 0.4 of that predicted from the value in O_2 assuming simple additivity, but this difference is possibly within the limits of error. The variation with electron energy and the order of magnitude of h are in agreement with Bailey's results for air. On the other hand, a rapid increase in h with increase in pressure at constant electron energy was found at low energy, while Bailey's results, which seem more reliable, show no variation with pressure. In H_2O h is of the same order of magnitude as in O_2, but in mixtures of H_2O and O_2 h is much larger than in either alone, showing that here at least the attachment process is complex.

Permanence of ions.—Evidence of the detachment of electrons from negative ions in oxygen at very high fields was found.

1. Introduction

THE work of Loeb,[1] Wahlin[2], and Bailey[3] has shown that, in many cases at least, the formation of negative ions from free electrons is a slow process, the electron making many collisions with gas molecules before finally becoming attached. The rate of ion formation is conveniently measured by the fraction of the collisions which result in attachment. We shall call this fraction the attachment coefficient and denote it by h. It is also the reciprocal of the average number of collisions made by an electron before becoming attached.

For a number of gases Loeb and Wahlin obtained approximate values of h. They range all the way from 0 for H_2 and N_2 to more than 10^{-3} (beyond the range of measurement) for Cl_2 and HCl. Their method was to measure the current between two plane parallel electrodes, one of which emitted photoelectrons, when a square wave, alternating voltage just insufficient to drive ions across in half a cycle was applied. This current obviously is a measure of how far the electrons go before attachment. From the latter and the electron mobility, h could be calculated. In some cases the mobility was measured in the same apparatus by the Rutherford alternating current method, and in some cases it was estimated.

* National Research Fellow.

[1] L. B. Loeb, Kinetic Theory of Gases, McGraw Hill, New York, 1927, p. 507; J. Frank. Inst. **197**, 45 (1924); Phil. Mag. **43**, 229 (1922).

[2] H. B. Wahlin, Phys. Rev. **19**, 173 (1922).

[3] V. A. Bailey, Phil. Mag. **50**, 825 (1925).

The quantity h has been measured as a function of the average electron energy by Bailey[3] in air and by Bailey and McGee[4] in NH_3. Bailey's method is to pass a mixed current of ions and electrons through a succession of slits in plane electrodes perpendicular to a uniform electric field. The fraction of the current passing one slit which also passes through the next is a measure of the rate of lateral diffusion and this in turn depends on the fraction of the current which is electronic, the electrons diffusing much more rapidly than the ions. The loss of electrons by attachment between one electrode and the next, together with the electron mobility, which is taken from the data of Townsend and Tizard[5] for air, gives h.

The present work is a study of the attachment coefficient h as a function of electron energy, gas pressure, and moisture content in air and oxygen. A new method is used. The results seem to be sufficiently new and interesting to warrant publication although their consistency and reliability leave much to be desired.

2. Principles of the Present Method

In Fig. 1, F is an oxide coated platinum filament emitting electrons which are driven downward by a uniform electric field. The gas pressure is higher than 6 mm. Hence the electrons on their way downward make many

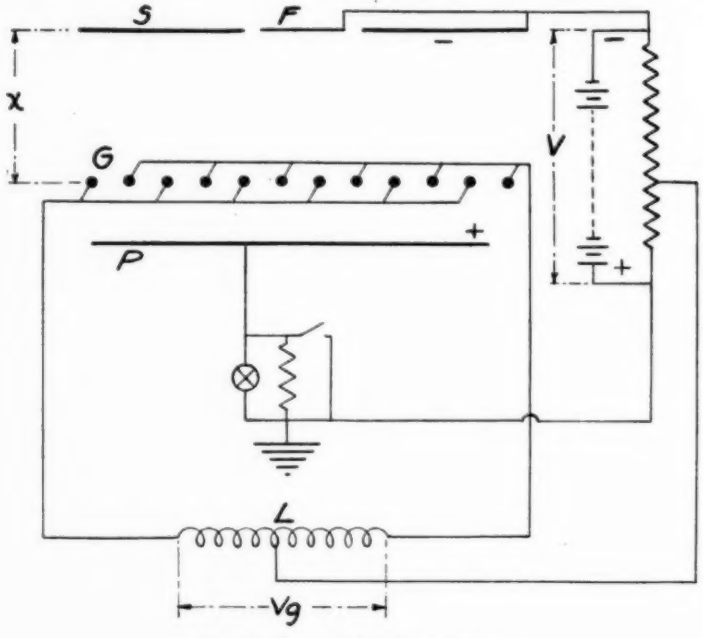


Fig. 1. Essentials of apparatus.

collisions with gas molecules and some attach to form ions. S is a plane electrode with a slit for the filament at its center. G is a grid of fine parallel

[4] Bailey and McGee, Phil. Mag. **6**, 1073 (1928).

[5] Townsend and Tizard, Proc. Roy. Soc. **A88**, 336 (1913); J. S. Townsend, J. Frank. Inst. **200**, 563 (1925).

wires (0.0080 cm diameter, spaced 0.1 cm apart). Alternate wires are connected to opposite ends of the coil L in which a high frequency voltage V_g can be induced. P is the collecting plate connected to the electrometer. With $V_g=0$, the fields above and below G are equal, the fine grid wires disturb the field but little, and both ions and electrons pass through the grid to P. When a sufficient alternating voltage is applied, the transverse field between adjacent wires removes the electrons, which have a high mobility, but does not affect the ions, which are too slow to move an appreciable distance before the field reverses. In practice, of course, some ions will be caught by the alternating field and some electrons will escape. When R, the ratio [(current received by the plate with a given V_g)/(current when $V_g=0$)],[4] is plotted as a function of V_g (Figs. 2a, 2b, and 2c) the curves

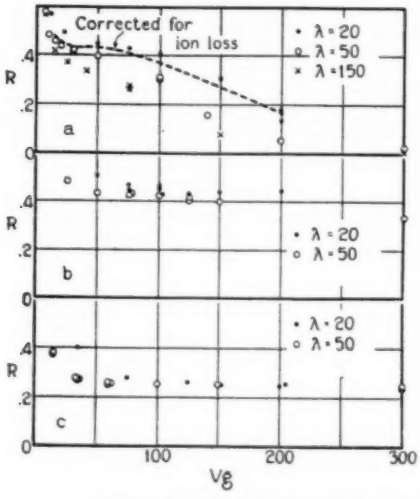


	Fig. 2a O_2	2b Air	2c 1.3%O_2 98.7%N_2
p	15 mm	60	100
X/p	1.05	0.89	0.12
R_i	0.42	0.42	0.26

Note improvement in curves with increasing pressure.

Figs. 2*a*, 2*b*, and 2*c*. Experimental curves of R against V_g. (λ = wavelength of high frequency V_g in meters.)

drop rapidly as V_g rises to the value at which nearly all electrons are captured, and then straighten out to a small slope caused by the capture of an increasing number of ions by the larger alternating fields. The ordinate at the point where the curve becomes straight, after a small correction for ion capture, gives R_i, the fraction of the electrons which have attached before reaching G. The ion loss correction is calculated from curves at high pressure where no electrons are present.

Let l be the mean free path of the electrons, v their average random speed W their average velocity in the direction of the electric field (drift velocity), x the distance from the source of electrons, measured parallel to the electric field, and I the current of *free electrons* at the distance x. The number of collisions an electron makes in going the distance dx in the direction of the field is $(v/lW)dx$. Hence the chance that an electron will attach in going the distance dx is $(hv/lW)dx$ and

$$dI/I=-(hv/lW)dx \quad \text{or} \quad ln(I/I_0)=-hvx/lW$$

$I/I_o=(1-R_i)$ is found experimentally. To eliminate v/l the mobility equation is used. It is

$$k=W/X=[83/(4\times 300)](el/mv)$$

where X is the field in volts per cm, e the electronic charge in e. s. u., and m the mass of the electron. The result is

$$h=-\frac{lW}{vx}ln(1-R_i)=\frac{4\times 300mW^2}{3Xex}ln(1-R_i)=\frac{4\times 300mk^2X}{3ex}ln(1-R_i).$$

Thus if the electronic mobility k, or its equivalent the velocity W in the direction of the electric field is known, h can be calculated. The values used for this calculation in the present work are those obtained by Townsend and Tizard[5] for air and by Brose[6] for O_2. For values of X/p below 0.5 in air (p = pressure in mm) W was extrapolated by Compton's mobility equation.[7]

It should be pointed out that values of the attachment coefficient obtained by all methods are subject to a good deal of uncertainty because of the unreliability of the electron mobility data. For instance, Bailey found a considerable discrepancy between his values of the electron energy in air as a function of X/p and those of Townsend and Tizard. This of course throws doubt on the values of W which were obtained at the same time as the energy values.

3. Apparatus and Procedure

The chamber containing the electrodes was of brass and had a ground joint made tight with dry shellac and sealing wax applied on the outside. Guard rings were used to secure uniform fields. In the first apparatus the electrodes were brass and copper, and the distance x from filament to grid was 5.51 cm. In the last apparatus the electrode surfaces were platinum and x was 2.80 cm. Before filling, the chamber was evacuated through a liquid air trap by a mercury vapor pump until after standing an hour or so with the pump off no discharge could be obtained in a discharge tube connected to a one inch spark coil. The last apparatus was heated to 115°C while being evacuated, which greatly hastened the liberation of water vapor from the large metal surface.

Air and oxygen were purified by passing slowly over hot copper oxide, sodium hydroxide, calcium chloride, and P_2O_5, each in 60 cm tubes, and finally through two liquid air traps. For N_2, the copper oxide was replaced by hot copper. The oxygen and nitrogen were obtained from ordinary commerical tanks. The system was clean enough so that no formation of negative ions was observable in nitrogen, even at 300 mm pressure, though an attachment coefficient 1/100 of that in air could have been measured.

4. Sources of Error

a. Uncertain electron mobility. This has already been pointed out.

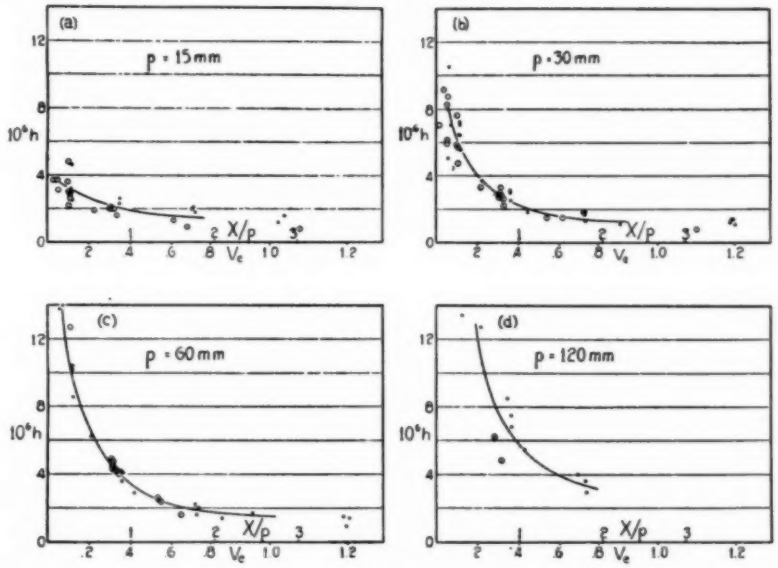
b. Excess attachment near filament. The assumption that attachment takes place at a uniform rate throughout the paths of the electrons from

[6] H. L. Brose, Phil. Mag. **50**, 536 (1925).

[7] K. T. Compton, Phys. Rev. **22**, 333 (1923); L. B. Loeb, Kinetic Theory of Gases, p. 503.

filament to grid can not of course be exactly true, for the electrons acquire their terminal energy only after travelling a certain distance in the field. However, at 15 mm pressure 90 percent of the terminal energy would be acquired within about 1/2 cm from the filament if the collisions between electrons and molecules were perfectly elastic, and since the energy loss is actually much more rapid, the steady state is reached much more quickly. For the experimental evidence see section 5a.

c. Diffusion of electrons to grid wires. In the absence of the alternating field the observed current is too small because some of the electrons diffuse to the grid wires instead of following the lines of force. This makes the observed value of h too large. A calculation of the error in h so introduced, using the usual mobility and diffusion laws, gives +100 percent at a pressure



Figs. 3*a*, 3*b*, 3*c*, and 3*d*. Attachment coefficient, h, in air. Circles and dots are experimental values with $x = 5.51$ cm and 2.80 cm respectively. (x is distance from filament to grid.) V_e = average electron energy in volts; X = field in volts per cm; p = pressure in mm.

of 11 mm and electron energies from 0.3 to 0.8 volts. This is too high, probably by a factor of at least 2, because at this pressure the electronic mean free path is about equal to the radius of the grid wires and hence the ordinary diffusion law no longer holds in the neighborhood of the wire (it gives infinite current density for an infinitesimal wire). The error is further reduced by the fact that nearly all measurements were made at pressures higher than 11 mm, and the error drops rapidly with increasing pressure.

d. Effect of change in current magnitude. In air and oxygen, change in the magnitude of the electron current caused by changing the filament current had no effect on R. In the mixture of 1.3 percent O_2 + 98.7 percent N_2 and in H_2O, an increase in current caused a decrease in R for which no explanation could be found. Hence no calculations can be based on the latter measurements.

e. The "hump effect." With low main field and rapid attachment, the curves of R against V_e showed an anomalous rise to a maximum at V_e from 50 to 150. The most reasonable explanation seems to be that some fault in the apparatus caused an alternating field at the filament which increased the electron current. The effect prevented measurements in weak fields, but is not believed to be an important source of error in the results presented.

f. Non-reproducibility. The discrepancies between measurements with different fillings of the same gas are sometimes large, particularly at weak fields (see Figs. 3a to 5d). They show no correlation with the rate of filling, length of time the chamber was heated and pumped before filling, or any other known factors. With few exceptions, the results with a given filling did not change appreciably on standing up to 7 days. A mixture of roughly 1 part oxygen and 4 parts nitrogen gave about the same result as air.

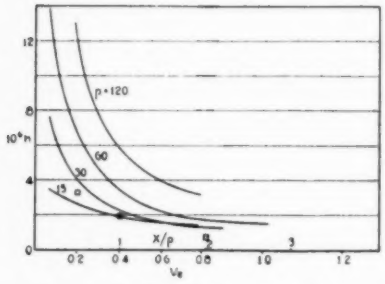
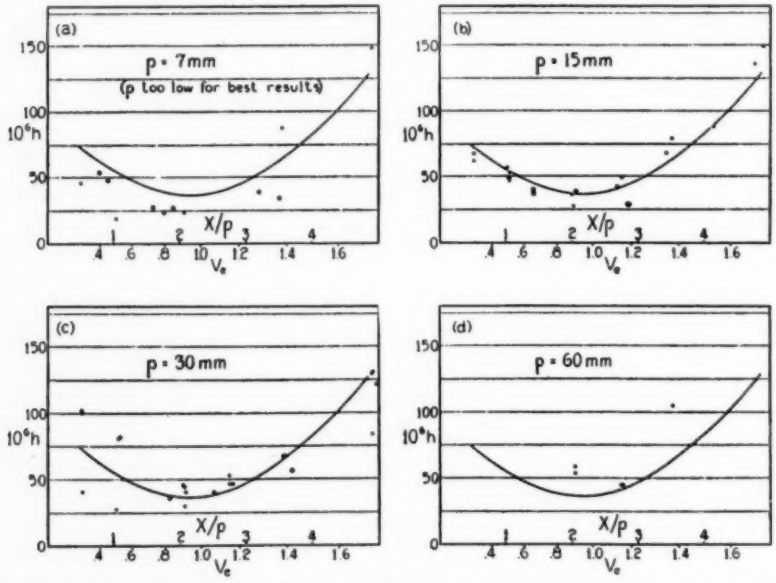


Fig. 4. Curves of Figs. 3*a* to 3*d* and results of Bailey, shown by squares, collected for comparison. V_e=average electron energy in volts; X=field in volts per cm; p=pressure in mm.

5. Results

Figs. 3a to 5d give the results of all determinations in air and oxygen. Points shown by circles were obtained with the older apparatus where the distance x from filament to grid was 5.51 cm. The solid points were obtained with the last apparatus in which x



Figs. 5*a*, 5*b*, 5*c*, and 5*d*. Attachment coefficient, h, in O_2. The curve is the same in all figures. Circles and dots are experimental values with x=5.51 cm and 2.80 cm respectively. (x is distance from filament to grid.) V_e=average electron energy in volts. X=field in volts per cm. p=pressure in mm.

was 2.80 cm, about half the previous value. The results for H_2O and for mixtures will be given only as rough comparisons of the attachment per cm of travel in the direction of the field, for h could not be calculated because of lack of knowledge of W or the electron mobility, and the measurements were too few in number to make exact quantitative figures of any significance.

a. Region in which attachment occurs. Permanence of ions. If the attachment took place primarily near the filament, or if a steady state were reached in which attachment were balanced by detachment, the two distances x would have given about the same values of R_i (R_i = fraction of electrons attaching before reaching grid), at the same values of p and X/p. Hence the values of h calculated for the larger distance x (shown by circles in Figs. 3a to 5d) would have been only about half as large as the values calculated for the smaller x. The fact that h is the same within the limits of experimental error, except at the lowest pressures where the electrons travel the largest distances before attaining their final energies, shows that attachment is a process taking place throughout the lives of the electrons as assumed, and that detachment is inappreciable in the main field.

b. Detachment of electrons from negative ions in high fields (violent collisions). The much stronger alternating field, on the other hand, seems to be able to cause detachment. The R curves in oxygen (e.g., Fig. 2a) fall off more and more steeply after V_g rises above about 50 volts. This must be due either to an abnormally high ion mobility, caused for instance by the breaking up of a cluster ion, or to detachment. If it were due to high ion mobility, it should be exaggerated by low frequency which increases the capture of ions, and curves taken at $\lambda = 150$ should fall about three times as fast as curves taken at $\lambda = 50$. This does not occur. (The principal reason that the curve for $\lambda = 20$ appears so much higher than the curve for $\lambda = 50$ is that the voltmeter reads about 20 percent too high at this high frequency, and the uncorrected readings are plotted. There is also a little "hump effect"). A certain amount of difference between the curves at different frequency is to be expected even in the case of detachment, for the lower frequency moves more ions into the region of strong field near the grid wires. Hence it appears that detachment rather than an increase of mobility which still remains of molecular order is taking place. When $V_g = 200$, the fields at the surface of a grid wire and half way between two wires are respectively 9000 and 1200 volts per cm. At a pressure of 15 mm the corresponding values of X/p are 600 and 80, giving 3.6 and 0.5 volts drop along one molecular mean free path. It is therefore not surprising to find detachment in the alternating field although none was found in the far weaker main direct field.

The air curves also show the abnormal drop in R at high V_g, but to a smaller extent as would be expected, for the higher total pressure reduces X/p, i.e., reduces the energy gain per free path. In H_2O detachment occurred less readily if at all. However, an addition of 4 percent H_2O to O_2, which was sufficient to double the attachment, did not greatly decrease the detachment.

c. Variation of h with average electron energy. In both air and oxygen h falls as X/p increases up to about 2, corresponding to 0.9 volts average electron energy. Bailey[3] found the same variation, his results being shown in Fig. 4. In oxygen h has a minimum at this value and then increases more and more rapidly as X/p rises. In air the results are not reliable at such high electron energies, because R_i was too small, but there may well be such a minimum. In ammonia Bailey and McGee[4] found an increase in h with increase in X/p. The variation with X/p indicates that in oxygen there are *two* processes of ion formation: one, dominant at low X/p, which gives out energy and so becomes less probable as the energy rises, and another, dominant at high X/p, which requires energy, and so becomes more probable as the number of electrons having the requisite energy increases with increasing X/p.

d. Variation of h with pressure. The values of h in air at low X/p are seen to rise rapidly with increase in pressure at constant X/p. The variation with pressure decreases as X/p increases. In oxygen the results disagree badly at low X/p, but there is some indication of the same variation as in air. Above $X/p=2$, which gives the minimum value of h, there is practically no variation with pressure. The variation with pressure is contrary to the results of Bailey who found that h was independent of pressure at constant X/p. To be sure he assumed this to start with, but he checked his assumptions by the agreement of the different values of h and of the electron energy (which is also given by his method) calculated from different pairs of pressures. An attempt to recalculate his results assuming a variation with pressure such as here observed shows that his method would really be quite sensitive in detecting such a variation. It is hard to find a reasonable cause for the difference between the present results and those of Bailey. Although all the sources of error in the present work which occur to the writer (diffusion of electrons to grid wires, detachment, excess attachment near filament, and impurities) would apparently produce a variation with pressure in the opposite direction to that observed, the greater consistency of Bailey's data and the simpler conditions in his apparatus justify greater confidence in his results. A variation of h with pressure at constant X/p is of course contrary to the hypothesis that attachment is a simple one stage process in which an electron strikes a single molecule and sticks to it permanently.

e. Comparison of h in air and oxygen. On the assumption that attachment consists simply in an electron striking a single molecule and sticking to it permanently, h depends only on the kind of molecule and the electronic energy, and the relative values of h in air and oxygen may be calculated as follows.

$$h_{\text{air}}=\frac{\text{number of attachments}}{\text{number of collisions}}.$$

Since $h_{N_2}=0$,

$$h_{air} = \frac{h_{O_2}\,(\text{number of collisions with } O_2)}{\text{number of collisions with } O_2 + \text{number of collisions with } N_2}$$

$$= \frac{h_{O_2} vnp/L_{O_2}}{vnp/L_{O_2} + v(1-n)p/L_{N_2}}$$

where $n = 0.2$ is the mol fraction of O_2 in air, p is the total pressure in mm, and L_{O_2} is the electronic mean free path in O_2 at 1 mm pressure. This gives

$$h_{O_2} = h_{air}(1 + 4L_{O_2}/L_{N_2}).$$

The results of this comparison, using values of L_{O_2} and L_{N_2} calculated from the mobility and electron energy, are shown in the table, the values of h_{O_2} so calculated from the measurements in air being given beside those actually measured in O_2. The former are less than half the latter. The combined errors in W, L, and the electronic energy coupled with the errors of the present work may well be responsible for the discrepancy. If a disagreement really exists, it shows that attachment is not the simple process assumed in this calculation. If results at the same total pressure instead of at the same partial pressure of oxygen had been compared, the discrepancy would have been more than 5 to 1.

TABLE I. *Relative values of h_{O_2} from measurements in air and oxygen at same electron energy V_e, and same partial pressure of oxygen, p_{O_2}.*

V_e volts	p_{O_2}	L_{O_2}	L_{N_2}	$10^6\, h_{O_2}$ from: air	oxygen
0.4	7	0.064	0.037	20	65
0.5	15	.064	.035	27	55
0.65	15	.062	.033	21	45
0.76	7	.061	.032	13	40
0.9	15	.059	.031	16	35

f. H_2O and mixtures containing H_2O. Definite evidence of the complexity of the attachment process, in some cases at least, is furnished by a few experiments in H_2O and mixtures of H_2O and O_2. H_2O alone gave roughly the same attachment per cm of travel in the direction of the field as O_2, but 4 percent H_2O added to O_2 doubled the attachment per cm, and 30 percent H_2O removed all trace of free electrons, which means that the attachment per cm was increased at least five fold. *Hence H_2O and O_2 co-operate in a complex attachment process which is much more efficient than the processes involving either alone.* On the other hand, 20 percent H_2O added to N_2 gave about the same attachment as 20 percent O_2 added to N_2.

The experimental work and most of the calculation was done at the Physical Laboratory of the University of California. The writer wishes to express his thanks to Professor Leonard B. Loeb, at whose suggestion this problem was undertaken, for his kind advice and criticism.

PRINCETON UNIVERSITY,
January, 1929.

THE SUN'S RADIAL MAGNETIC GRADIENT AND ATMOSPHERE

By Ross Gunn

Abstract

Theory of the radial magnetic gradient of the sun based on the diamagnetic effect produced by ions spiralling about the impressed magnetic field.—The thermal ionization of the sun's atmosphere, free paths and velocities of thermal agitation of the molecules and ions all have such values that the diamagnetic effect is very large in the regions of the sun's atmosphere where abnomally large magnetic gradients are observed. Extrapolation of the diamagnetic effect into regions where there are no available experimental data shows that the magnetic field at the surface of the sun is several times the generally accepted value.

Ionic densities estimated from magnetic data.—These agree well with data from other sources. The mean atomic weight of the particles in the sun's atmosphere assuming it to be in purely gravitational equilibrium is found to be approximately 3.3 or when a correction is made for the presence of an electric charge on the sun this becomes 5.5.

SPECTROSCOPIC researches at Mt. Wilson Observatory[1] have shown that the sun possesses a general magnetic field which is similar in many respects to that of the earth. The magnetic field in the sun's atmosphere has been studied by means of the Zeeman shift of certain spectral lines which are known to originate at definite altitudes above the photosphere. These researches indicate that the sun's magnetic poles bear the same relation to its rotation as those of the earth. Moreover, at any given layer in the sun's atmosphere the distribution of magnetization is nearly the same as that on the earth and corresponds roughly to the field produced by a uniformly magnetized sphere. It has been possible to determine the magnetic field as a function of the altitude above the photosphere and the available data have been plotted in the form of a smooth curve in Figure 1. This curve will be used in the present paper for the purpose of computation.

The outstanding characteristic of the sun's general magnetic field is the rapid radial diminution of its resultant intensity, which falls from 55 gauss at a level of 250 km above the photosphere to 10 gauss at 450 km. Such a gradient is approximately 7000 times as great as would be expected if the sun were a uniformly magnetized sphere whose polar field strength is 55 gauss. A great difficulty of solar theories has been to explain the general magnetic field and at the same time to account for the rapid radial gradient which occurs in the reversing layer. The results of the present paper show that the radial gradient is a secondary phenomenon associated with the high temperature and ionization of the sun's atmosphere, and the presence of the gradient places no restrictions on the theory of the general field. A

[1] Hale, Astrophys. J. **38**, 31 (1913), Hale, Seares, van Maanen and Ellerman, Astrophys. J. **47**, 1 (1918).

consistent view of the sun's and earth's permanent magnetic field is therefore possible.

In a recent paper[2] the writer pointed out that, under certain conditions of ionization, temperature, pressure and magnetic field, a true diamagnetic effect exists which is due to the motion of ions or electrons spiralling about the impressed magnetic field. An examination of magnitudes with such spectroscopic data as are now available indicated that conditions on the sun in the region of large magnetic gradient are precisely those most favorable

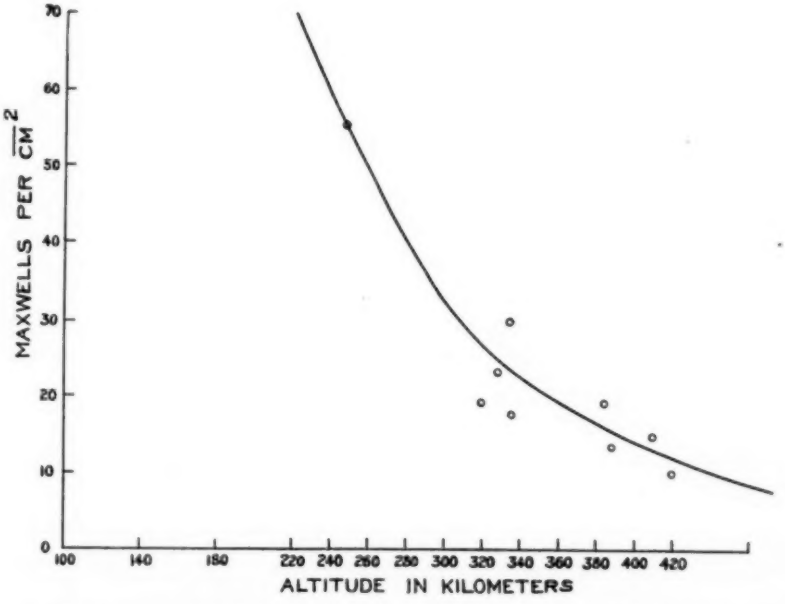


Fig. 1. Magnetic field as a function of altitude above the photosphere. Plot of available data

for a large diamagnetic effect.[3] In previous work it was shown that a large diamagnetic effect existed when the free path of the ion is greater than the radius of the helix generated by the ion when acting under the influence of thermal agitation and the magnetic field. This condition exists in the sun at altitudes corresponding to regions of large observed magnetic gradient.

The radius of the spiral generated by the ion moving in the magnetic field is obtained by equating the centrifugal and magnetic forces, and if we express the velocity of the ion in terms of absolute temperature we have

$$r=(3mkT)^{1/2}/eB \tag{1}$$

where r is the radius of the circle generated by the ion, m the mass of the ion, e its charge, B the magnetic field impressed on the ion, k the Boltzmann constant and T the absolute temperature. The gases of the sun will be

[2] Gunn, Phys. Rev. **32,** 133 (1928).

[3] Gunn, Note on the radial magnetic gradient of the sun, Science, p. 273 (Sept. 21, 1928).

[4] Saha, Phil. Mag. **40,** 472 (1920).

largely ionized by the high temperatures and if we compute the fractional ionization according to the relations of Saha,[4] we find that to a first approximation we may assume the entire gaseous body to be singly ionized. Moreover, we shall assume that each cm³ is nearly neutral electrically and that no radial electric field on the sun exceeds that predicted by the theory of Pannekoek[5] which takes account of the gravitational separation of the light electrons from the heavier positive ions. This theory indicates that the sun carries a positive charge of 10^{12} e.s.u. which produces an electric field near the surface of the sun of at least 6×10^{-8} volts/cm.

It has been shown[2] that the diamagnetic intensity of magnetization, I, for long free paths is given by

$$I=-NkT/B \tag{2}$$

where N is the number of ions per cm³, k the Boltzmann constant, T the absolute temperature and B the magnetic field impressed on the spiralling electrons. This relation has been deduced on the assumption of long free paths and if N is large and the free paths are long the diamagnetism of any region may be large. In order to examine whether the condition of long free paths is satisfied we must determine the kinetic theory values for the length of the free paths. The free path (λ) of an ion is given by

$$\lambda_i=1/2^{1/2}\pi\sigma^2N \tag{3}$$

and for an electron

$$\lambda_e=4/\pi\sigma^2N \tag{4}$$

where σ is the kinetic-theory diameter of the molecules or ions. Since the free path of the electron is greater for a given molecular density diamagnetism due to electrons will persist at somewhat higher pressures than for ions. In order to establish the length of free path which certainly yields a strong diamagnetic effect we have assumed arbitrarily that the critical free path was equal to the radius of the helix generated by the ion. It seems probable that this critical free path is nearly a hundred times longer than the shortest allowable path, but the present assumption is certainly safe and will therefore be used.

The molecular density corresponding to the critical free path may then be determined by equating equations (4) and (1), which yields

$$N(\text{critical})=\frac{4eB}{\pi\sigma^2(3mkT)^{1/2}} \tag{5}$$

Thus we have a criterion for the existence of the diamagnetic effect, for if N is less than N(critical) the free paths are long and the resulting effect large. Putting in appropriate values for the constants of Eq. (5) on the sun,

[5] A. Pannekoek, Astro. Inst. Netherlands, No. 19 (1922).

namely $e=1.57\times10^{-20}$ e.m.u. $\sigma=2\times10^{-8}$ cm; $m=10^{-27}$ grams; $k=1.37\times10^{-16}$; $T=6000°$; we have

$$N\text{ (critical, sun)}=1.2\times10^{15}\cdot B \tag{6}$$

Turning our attention to the experimental data of Fig. 1, we observe by aid of Eq. (6) that an ion density of 10^{16} ions is allowable at an altitude of 425 km and 5×10^{17} ions/cm^3 at 250 km without violating the condition of long free path.

The determination of the ionic densities from spectroscopic pressure shift, absorption, etc., in the region under consideration by St. John and Babcock,[6] Russell,[7] Stewart,[8] and Fowler and Milne,[9] all point to an ion density of about 10^{16} or 10^{17} which increases to 10,[10] perhaps, directly at the photosphere. These determinations are very difficult and are subject to wide variations and can therefore only be considered tentative.

If we accept the values above which are seen to satisfy the requirement regarding free paths and compute by aid of Eq. (2) the intensity of magnetization substituting in known values for B and T; it turns out that I is absurdly large compared to the resultant observed field. The assumed ionic densities must therefore be too large for N is the only quantity which is not observed directly. We are led to the conclusion that the lower lying layers of the sun's atmosphere are strongly diamagnetic and shield the upper layers by their magnetic action. This shielding effect makes it very difficult to specify the magnitude of the impressed field at any given point.

Certain energy relations give a clue to the value of intensity of magnetization in terms of the resultant field B. Consider a region which impresses a constant magnetic field H upon rings of electrons having a total magnetic moment M. The energy U necessary to line up the electron rings with the impressed field is given by

$$U=-M\cdot H \tag{7}$$

or the energy per unit volume u

$$u=-I\cdot H \tag{8}$$

In addition to this relation we have the usual relation which gives the energy resident in the medium.

$$u'=BH/8\pi \tag{9}$$

With the exception of the radial variation, the field about any given region may be taken to be symmetrical and therefore the energy resident in the medium may be taken as somewhat less than the energy producing the magnetic effect. That is $u>u'$ or

[6] St. John and Babcock, Astrophys. J. **60**, 323 (1924).
[7] Russell, Astrophys. J. **55**, 135 (1922).
[8] Stewart, Phys. Rev. **22**, 324 (1923).
[9] Fowler and Milne, Royal Astron. Soc. Monthly Notices, **83**, 402 (1923).

$$I \cdot H \geqq BH/8\pi. \tag{10}$$

Substituting for the value of I we have by aid of (5)

$$\frac{4eB}{\pi\sigma^2(3mkT)^{1/2}} \geqq N \geqq \frac{B^2}{8\pi kT}. \tag{11}$$

Numerical considerations have lead to the conclusion that the facts would be best represented by assuming that $B = 4\pi I$ or

$$N \doteq B^2/4\pi kT \tag{12}$$

which satisfies (11) and permits at once an estimate of the ion density of the diamagnetic atmosphere of the sun.

Since B is known from observational data the ionic densities may be computed by aid of Fig. 1 and equation (12). The results of these calculations assuming T constant at 6000° are plotted in Fig. 2. The curve gives the approximate ionic densities which exist at various altitudes above the

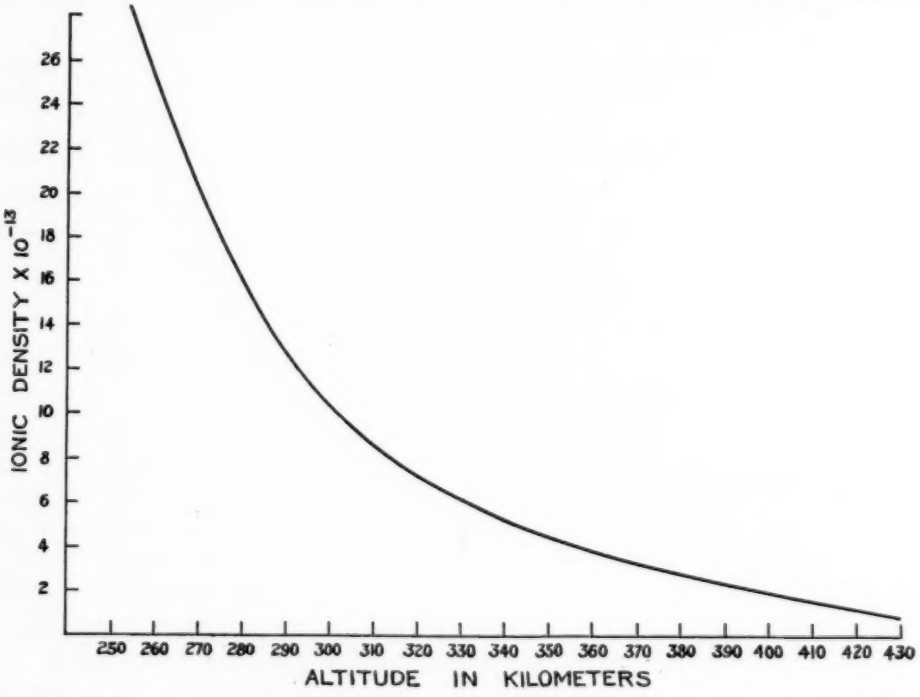


Fig. 2. Computed values of ionic density as function of altitude above the photosphere.

sun's photosphere based on the assumption that the observed effects are due to diamagnetism. Within the limit of experimental error the curve of Fig. 2 is logarithmic and it has been possible to determine the effective mean atomic weight of the particles in the reversing layer. We shall assume the atmosphere to be in purely gravitational equilibrium and may therefore express the ionic density at any level by

$$N = N_0 \exp(-Zm_H gh/RT) \tag{13}$$

where N_0 is the number of ions at the photosphere, N the number of ions per cm³ at a distance h above the photosphere, Z the apparent atomic weight, M_H the mass of a hydrogen atom, R the gas constant, T the absolute temperature and g the acceleration due to gravity. We find on applying the above relation to the data of Fig. 2, that the relation is satisfied throughout the region of observed data for $Z=3.3$ and $N_0=2\times10^{17}$ ions/cm.[3] Eddington concludes that in the interior of a star the most probable value for Z is about 2.2. In regions on the surface of a star marked deviations are to be expected and indeed the value we find is too small rather than too large. Pannekoek's work[5] indicates that there must be a slight radial electric field on the sun and if it exists it will be in such a direction that the electric field will tend to support the positive ions while the electrons will be subject to electric forces which will urge them downward. Since the mass of an electron is negligible compared to the mass of an ion, the contribution to the density is overwhelmingly due to the ions and if we take the value of the field computed by Pannekoek; namely, 6.0×10^{-8} volts/cm, and correct for the electrical forces this introduces on each ion, we secure a value for Z of 5.5. It is perhaps well to point out that since Z is the mean atomic weight of the particles and since on the average there are nearly as many electrons as ions the average atomic weight of the positive ions alone will be 6.6 and 11.0 respectively according to forces assumed to act on the ions.

An estimate of the magnetic field intensity at the photosphere has been made assuming that diamagnetism plays an important part down to the photosphere proper as, indeed, is indicated by the present discussion. The substitution of N_0 in equation (12) gives a value of B at the surface of 400 maxwells/cm.[2] The estimates of ion densities derived in this paper are in substantial agreement with those determined spectroscopically and lends considerable support to the view that the diamagnetism of ions and electrons plays an important part in magnetic phenomena associated with the sun and earth. A volume distribution of diamagnetism of the type which has just been considered accounts definitely for the observed magnetic gradient of the sun and seems to indicate that its magnetic moment is several times greater than the commonly accepted value.

ADDENDUM—February 2, 1929. A paper on the above subject by S. Chapman[10] has just appeared in which he attributes the limitation of the sun's field to eastward gravitational currents flowing in the ionized layer. A consideration of this phenomenon has led Chapman to nearly the same relation between magnetic field strength and ion density as has been found in the present paper. (Compare his equation 31 with 11 above.) The two views, therefore, predict the same reduction in field strength and if eastward currents actually exist the net effect must be considered as being due to both causes. A new electromagnetic effect arising from the drift motion imposed on ions spiralling about in homogeneous magnetic fields has been found by the

[10] S. Chapman, Monthly Notices. Roy. Astro. Soc., Nov., 1928.

writer and this effect predicts a westward current of the same order of magnitude as the eastward current studied by Chapman. It is yet too early to deny the existence of an eastward current since the data now available regarding the constitution and distribution of the sun's atmosphere are incomplete. In his discussion, Chapman has taken unusual liberty with the observed data for he has assumed that the major portion of the sun's field has vanished in a layer depth of 19 km whereas measurements at Mount Wilson Observatory indicate that this change takes place in 190 km. The numerical calculations in the present paper are based on Mount Wilson data. A discussion of the new effect that produces the westward current referred to above and its application to the magnetic fields associated with sunspots, the sun and earth, has been prepared and should appear shortly.

NAVAL RESEARCH LABORATORY,
WASHINGTON, D. C.
January 3, 1929.

MAGNETIC LOSSES OF IRON IN HIGH FREQUENCY ALTERNATING CURRENT FIELDS

By John R. Martin

Abstract

A number of investigators have studied the power loss due to eddy currents and hysteresis in iron when placed in high frequency alternating current fields, but the results obtained are in wide disagreement. Using a new method, the author has investigated the variation of this loss with the frequency for several areas of cross section. The total loss is considered as that due to an equivalent resistance and by measuring the values of this resistance at resonance, the loss may be determined from the I^2R relation. With magnetizing currents of 3, 4 and 5 ampere-turns per cm, the measurements are made on short iron cylinders of various areas of cross section at frequencies ranging from 520 to 968 kilocycles. The loss is found to increase with frequency in the small samples and to decrease with frequency in the larger. At any particular frequency the loss per unit volume is less the greater the area. This is due to the magnetic shielding effects of eddy currents in the large samples and the disagreement between previous investigations may thus be explained.

THE results obtained by a number of investigators who have studied the losses due to eddy currents and hysteresis in iron when placed in high frequency alternating current fields are in wide disagreement. Corbino[1], Alexanderson[2], Wilson[3], and others have found increasing losses with increasing frequencies; Tankadate[4], Weihe[5], and Nusbaum[6] have found decreasing losses with increasing frequencies, while Hopkinson[7], Gray[8] and Maurain[9] have obtained results indicating that the energy loss per cycle is independent of the frequency. An excellent resume of the principal work done in this field from 1827 to 1923 has been given by Bown.[10]

This paper describes a new method for determining the combined losses due to eddy currents and hysteresis, and gives the results obtained for certain specimens of soft iron at frequencies from 520 to 968 kilocycles. Three values of magnetizing current are used, and the total loss as a function of the frequency, the magnetizing current and the cross-sectional area are indicated.

Theory of the Method

The method used in this investigation is based on the assumption that the combined loss due to eddy currents and hysteresis may be considered as

[1] O. M. Corbino, Phys. Zeits. **6,** 64 (1905).
[2] E. F. W. Alexanderson, Trans. A.I.E.E. **30,** 2433 (1911).
[4] L. T. Wilson, Inst. Rad. Eng. Proc. **9,** 56 (1921).
[4] A. Tankadate, Phil. Mag. **28,** 207 (1889).
[5] F. A. Weihe, Wied. Ann. **61,** 578 (1897).
[6] C. Nusbaum, Inst. Rad. Eng. Proc. **7,** 15 (1919).
[7] J. Hopkinson and B. Hopkinson, Electrician **29,** 510 (1892).
[8] T. Gray, Phil. Trans. **184,** 531 (1892).
[9] C. Maurain, Jour. de Phys. **7,** 461 (1898).
[10] R. Bown, Jour. Frank. Inst. **183,** 41 (1917).

the equivalent of a pure resistance inserted in an oscillating circuit, in which energy is absorbed at the same rate as in the iron. If then, the resistance of the oscillating circuit is measured at resonance, first with the iron sample inserted in the magnetizing coil, and again with the iron removed, the difference between these two values will give the value of the "equivalent resistance." Thus, calling the circuit resistance with the sample in the coil R_1 and without the sample R_2, the magnetizing current I and the equivalent resistance of the losses X, we have

$$X = R_1 - R_2$$

and the power loss

$$P = I^2 X$$

the same magnetizing current being used for both cases.

The problem therefore resolves itself into the problem of the accurate measurement of the change of the resistance of a circuit at high frequencies due to the insertion of an iron sample in the magnetizing coil, and the variation of this change of resistance with frequency and with the physical dimensions of the sample. The power loss for various values of magnetizing current may then be determined from the I^2R relation.

The assumption thus made is similar to those made in other determinations of power loss at high frequencies, such as the "series resistance" of a condenser, the "radiation resistance" of an antenna, etc.

Measurement Method and Apparatus

The familiar "resistance variation" method was used for measuring the circuital resistance, the measurement and power circuits being shown in Figure 1. The power circuit is a vacuum tube oscillator using a 50 watt tube supplied with 500 volts from a motor generator, the frequency being controlled by a condenser C_1. The power circuit is coupled to the measurement circuit through a single turn coil, and also to an accurately tuned wave-meter for indicating the frequency of the oscillations. The measurement circuit consists of a magnetizing coil, a standard tuning condenser, milliammeter, and a special switch for inserting the standard resistances. A single layer solenoid of 70 turns wound on a glass form was used as a magnetizing coil, with a large ratio of length to diameter in order that the magnetizing field might be as uniform as possible. Calculation of the strength of field for various points along the axis of the coil shows that a length of sample of 4 cm can be used, and this length was used for all samples. The standard resistances consist of manganin strips of equal lengths and of a small enough diameter that the variation of resistance due to skin effect may be considered negligible for the range of frequencies used. For easy removal of the magnetizing coil and the standard resistances a special switch similar to that used by Dellinger and Preston[11] in their deter-

[11] J. H. Dellinger and J. L. Preston, Bureau of Standards Sci. Paper No. 471 (1923).

mination of dielectric losses was used. A thermocouple milliammeter was used for indicating the value of the magnetizing current, and the measurement circuit was tuned with a precision type condenser.

This circuit was very carefully shielded to guard against stray electromotive forces, and the utmost precautions were used to prevent interaction

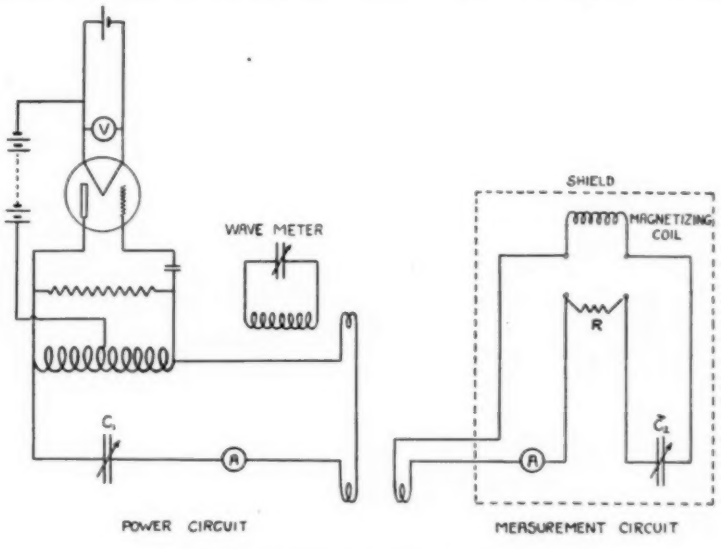


Fig. 1. Diagram of electrical circuit.

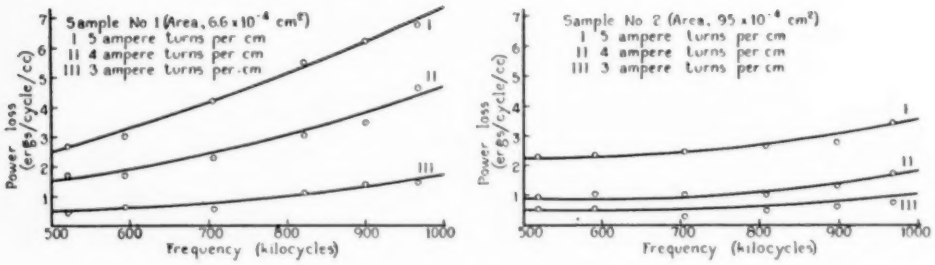
between the measurement and power circuits. The minimum coupling necessary to give the desired magnitude of current was used, and at all times during the measurements the circuits were carefully checked to see that no interaction took place.

Method of Observation

In making the measurements the oscillator was set at the desired frequency as determined by the wave meter. The measurement circuit was then tuned to resonance, and the coupling adjusted until there was no reaction of the measurement circuit on the power circuit. The magnetizing current was then adjusted to the desired value by varying the oscillator plate voltage, and the circuits again checked for absence of reaction. The circuital resistance was then determined by inserting three values of resistance, the current for each inserted resistance and for zero inserted resistance being observed. The observation was then repeated and the results averaged. The sample was then inserted in the magnetizing coil, and after readjusting the power circuit, the observations were repeated as before. The difference between the two values obtained for the circuital resistance is taken as the value of the equivalent absorbing resistance of the sample.

The observations were made on three different samples of low carbon iron drawn from the same ingot, of areas 6.6×10^{-4}, 95.0×10^{-4}, and 630.0×10^{-4} cm^2 and of length 4 cm in each case. The samples were sealed in small glass tubes and were accurately centered along the transverse axis of the coil.

The measurements were made on each sample at frequencies of 520, 592, 706, 810, 900, and 968 kilocycles per second, using magnetizing currents of 3, 4, and 5 ampere turns per cm.


Sample No 1 (Area, 6.6 x 10⁻⁴ cm²)
I 5 ampere turns per cm
II 4 ampere turns per cm
III 3 ampere turns per cm
Power loss (ergs/cycle/cc)
Frequency (kilocycles)
Sample No 2 (Area, 9.5 x 10⁻⁴ cm²)
I 5 ampere turns per cm
II 4 ampere turns per cm
III 3 ampere turns per cm
Power loss (ergs/cycle/cc)
Frequency (kilocycles)

Figs. 2. and 3. Power loss as function of frequency.

From the data thus secured, the loss in terms of ergs per cycle per cubic centimeter was determined for the samples with the frequencies and magnetizing currents stated. The results are shown in Figs. 2, 3 and 4.

Conclusions

In calculating the power loss from the measured values of the resistance, there is some question as to the proper value of current to consider as the magnetization current since by the very nature of the resistance-variation method, the current is a variable. In each case the current for zero inserted resistance was used for the I^2 factor. The difference is however small and did not seem to alter the results appreciably. The general variation as shown by the curves is indicated without a doubt.

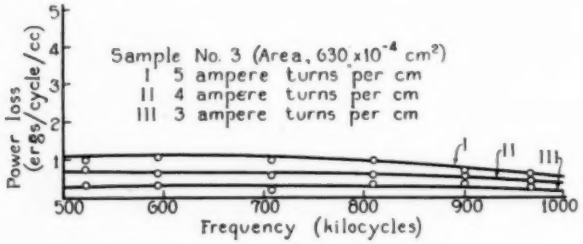

Sample No. 3 (Area, 6.30 x 10⁻⁴ cm²)
I 5 ampere turns per cm
II 4 ampere turns per cm
III 3 ampere turns per cm
Power loss (ergs/cycle/cc)
Frequency (kilocycles)

Fig. 4. Power loss as function of frequency.

The results indicate that the energy loss per cycle per unit volume is a function of the frequency, the magnetizing current, and the area of cross section. The loss seems to increase with the frequency for the smaller cross sectional areas, and to remain constant or to decrease slightly with the larger cross sectional area. This variation is probably due to the shielding effect of eddy currents, and explains the disagreement in the results of previous investigators.

Case School of Applied Science,
Cleveland, Ohio,
October 23, 1928.

ABSORPTION SPECTRUM OF LIQUID BENZENE: A CRITICISM OF A PAPER BEARING THIS TITLE BY BARNES AND FULWEILER

By Joseph W. Ellis

Abstract

Is is shown that the assumption by Barnes and Fulweiler of a constant amplitude of vibration for all stationary states of an anharmonic oscillator is theoretically unsound. It is also pointed out that the precision of these authors' measurements on four bands in the visible and near infra-red absorption spectra of liquid benzene cannot be used as a test for the superiority of the new wave-mechanics over the classical quantum theory.

IN A recent issue of this journal Professor Barnes and Mr. Fulweiler[1] presented the results of their measurement of wave-length positions of two near infra-red and two visible absorption bands of liquid benzene. Their conclusion that these four absorption maxima represent the second, third, fourth and fifth overtones of a fundamental band near 3.3μ took no cognizance of the fact that the present writer[2] presented the same conclusion in the same journal eight months earlier.

The determinations by Barnes and Fulweiler of the wave-length values of these bands, which are not new, are without doubt the most accurate of all observations which have been made upon them. It is doubtful, however, if any degree of accuracy can serve to determine whether the new wave-mechanics or the classical quantum theory is superior in yielding a formula for the arrangement of these four bands into a frequency series.

In their theoretical treatment of the subject these authors present an argument designed to show that this series of bands must be represented by a band formula in which the quantum numbers are odd multiples of 1/2. The assumption in their argument is theoretically unsound as the following considerations will show.

The bands are shown to fit very accurately the usual equation for the frequency absorbed by an anharmonic oscillator:

$$\nu_n = \omega_0 n - \omega_0 x n^2 \tag{1}$$

But as an approximation, since x is small, the authors consider a harmonic oscillator, quantizing the energy with the restricting condition that the amplitude of the vibration be the same for the different quantum states and invoking the selection rule that it change by only one unit. This gives the relation

$$\nu = (2n_0+1)h/2\pi^2 m x_0^2 \tag{2}$$

which the authors apparently assume should approximately represent the series of bands in question, "except for the small correction term on account of the oscillator vibrating anharmonically." This it cannot possibly do for it

[1] Barnes and Fulweiler, Phys. Rev. **32**, 618 (1928).
[2] Ellis, Phys. Rev. **31**, 310 (1928).

requires an entirely different type of absorbing mechanism from the anharmonic (or harmonic) oscillator, which has so far been entirely successful in representing the facts. First, the assumption that all states possess the same amplitude requires that the energy changes be ascribed to an increase in the binding force, that is, to an increase in the coefficient of the squared term in the potential energy function. This requires that the frequency of oscillation increase toward the higher quantum states, and the transitions must be thought of as changes from one harmonic oscillator to another with a different force coefficient or potential energy function. Such a change in the binding force must be ascribed to an electronic change, and it is evident that, in general, there must be an additional amount of energy supplied for this purpose. No provision is made for this, however.

Secondly, the restriction that Δn must equal unity requires that each band originate on different energy levels, whereas, for the anharmonic oscillator the level is common to all the bands. Theoretically, then, relation (2) holds for quite a different type of absorbing mechanism from that to which the anharmonic relation applies. It is apparent, therefore, that this relation can supply no information regarding the use of half or integral quantum numbers for this type of oscillator.

In addition it is interesting to note that Czerny[3] in his examination of the vibration-rotation bands of HCl gas, points out that an anharmonic series of bands cannot be employed to test the superiority of either of the two quantum theories. Each fits the observed data equally well, the only difference being that different values for certain molecular constants, such as the moment of inertia and the fundamental vibration rate, are obtained. Until some independent method of checking these constants is arrived at no choice can be made between the two theories in their applications to the anharmonic vibrator.

The wave-mechanics gives for the energy of such a vibrator in its n^{th} state

$$E_n=(n+\tfrac{1}{2})h\omega_0-(n+\tfrac{1}{2})^2h\omega_0x \tag{3}$$

Writing a corresponding expression for the n'^{th} state and subtracting it from that for the n^{th} state, one gets for the frequency absorbed

$$\nu_{(n-n')}=(E_n-E_{n'})/h=(n-n')(1-x)\omega_0-(n^2-n'^2)\omega_0x \tag{4}$$

In typical infra-red absorption spectra the initial state, represented here by n', equals zero. Under this condition Eq. (4) becomes

$$\nu_n=(1-x)\omega_0n-\omega_0xn^2 \tag{5}$$

Thus the wave-mechanics also yields an equation of the form (1). The only difference is that the vibration frequency ω_0 calculated by means of Eq. (5) is slightly higher than its value obtained from Eq. (1). Quantum numbers are still integers. The 1/2 term enters only in the energy expression and is interpreted by Czerny as indicating an initial vibration in the oscillator.

UNIVERSITY OF CALIFORNIA AT LOS ANGELES,
December 3, 1928.

[3] Czerny, Zeits. f. Physik **45**, 476 (1927).

ABSORPTION SPECTRUM OF LIQUID BENZENE: REPLY TO THE FOREGOING CRITICISM BY ELLIS

By James Barnes

SIX months earlier than Professor Ellis' abstract[1] I published with Mr. Fulweiler an article[2] in which we reported that we had photographed and measured two strong absorption bands of benzene at 8741A and 7134A and said that "no absorption was found at wave-lengths 0.835μ and 0.760μ." These latter bands were at that time an integral part of Ellis' anharmonic series due to the C−H group. No mention of our results is made in the above abstract by Ellis, although the values of the wave-length of two of the bands agree exactly with our values. It was the strong intensity of these bands, the accurate measurement of their wave-lengths, the elimination of bands at 0.834μ and 0.760μ and the measurement of the band at 6060A shortly afterwards, that gave us the clue to the series and which led us to extend our work in the region greater than 1μ.

I hold no brief for the assumption under criticism except that it seems to fit in with the data obtained. There is no violation of the idea in wave mechanics that the 1/2 term indicates an initial energy state of the oscillator and that quantum numbers, as used by Ellis, are integers.

January 16, 1929.

[1] Ellis, Phys. Rev. **31**, 310 (1928).
[2] Barnes and Fulweiler, Jour. Am. Chem. Soc. **49**, 2034 (1927).

BOOK REVIEWS

Müller-Pouillets, Lehrbuch der Physik, 11 Auflage, Fünfter Band, Erste Hälfte Physik der Erde, Pp. 840, figs. 341. Friedrich Vieweg, Braunschweig, 1928. Price unbound, RM 49.

The volume is well printed on good paper with a flimsey paper cover. The chapters, which were practically all written before 1926, are as follows: meteorology, acoustics of the atmosphere, optics of the atmosphere, physics of the sea, physics of glaciers, terrestrial magnetism, the aurora, atmospheric electricity, mechanics and thermodynamics of the body of the earth (Erdkörpers). The resumés of the various subjects are excellent, the descriptions of experimental methods, facts of observation and theories being maintained in proper balance. The chapter on the acoustics of the atmosphere was the first which the reviewer has seen of a promising and little touched field. There is a slight emphasis on German references, often well deserved, and occasionally the conclusions are invested with an air of completeness and finality more appropriate to an elementary text than to an advanced treatise.

E. O. HULBURT

Handbuch der Experimentalphysik. WIEN AND HARMS. Vol. XV. **Radioaktivität.** K. W. F. KOHLRAUSCH. Pp. 885, figs. 285. Akademische Verlagsgesellschaft m. b. H., Leipzig, 1928. Price unbound, RM 79.

The author of this volume on radioactivity is well known for his contributions in the study of γ-rays. The material in the book includes results of 1927, at least partially, and is therefore quite up to date. It is divided into logical sections. After a brief historical and general survey of the subject, the quite extensive chapters on γ-rays, β-rays and α-rays follow, each dealing with the physical properties of, the ionization effects by, and the theoretical consideration bearing on, the radiation in question. These are followed by shorter chapters on recoil radiation; on various effects of the radiation on matter, inert and living; on the radioactive disintegration theory, the constants and the various relations and laws involved. Longer chapters follow on the methods and instruments used in the measurements and on the radioactive series. The concluding chapter deals with the atomic nucleus, bringing together the experimental facts from studies in radioactivity and in artificial disintegration of atoms as well and discussing the hypotheses advanced which relate to the structure of the nucleus. Tables include atomic constants and various data relating to the properties of the rays and their effects. An index of reference to the various formulae and an index to the various tables are given preceding the customary indices of subjects and of authors. The references are given as footnotes on each of the pages where used. Errors discovered in proof-reading are noted at the beginning of the book. As a volume dealing with the subject of radioactivity it is comprehensive and well written and as up to date as books can be.

ALOIS F. KOVARIK

Spectroscopy of the extreme ultra-violet. THEODORE LYMAN. 2nd Edition. Pp. 160, fig. 7. Longmans, Green and Company, New York, 1929. Price $3.75.

The second edition of this well-known monograph on the extreme ultra-violet region of the spectrum is a thorough revision of the earlier edition. Over one-half of the text has been completely rewritten to include the many advances that have been made in this field during the last fifteen years. However, the plan of the book has been left unchanged and the subjects treated have been confined to those discussed in the original volume. Thus the author has limited the text to experimental methods and results and has not attempted to discuss the many theories of atomic and molecular structure that have been obtained from an analysis of the spectra in this region.

There are chapters on such subjects as, apparatus for the study of the extreme ultra-violet, absorbing and reflecting powers of various substances in this region, and the emission

spectra of the elements that have been studied. In general, the discussions are thorough and the references to original sources complete. Tables of the emission spectra of several of the commoner elements are given at the end of the volume.

A treatise on any field is always welcome when it comes from one who has played as large a role in the development of the field as Professor Lyman has in the opening up of this region of the spectrum. It is doubly welcome when it is written with a care that characterizes the present volume.

I. S. BOWEN

Geologie und Radioaktivität. GERHARD KIRSCH. Pp. 214, figs. 48, tables 31. Julius Springer, Berlin, 1928. Price unbound, RM 16.

Twenty years after the appearance of Joly's epoch making book of the same title it is fitting that an account should be taken to evaluate the contributions of this newest branch of geology and geophysics. This has been accomplished by Kirsch with searching thoroughness and without depriving the subject of any of that intriguing appeal originally imparted to it by Joly, Strutt, Rutherford and its other pioneer investigators.

The two principal contributions which radioactivity has brought to geology are: (1) a new, large and unsuspected source of internal terrestrial heat which, through its universal and continuous action, presents the necessity of completely revolutionizing theories of the tectonic changes in the earth's crust; (2) a genetic relationship between certain heavy elements which not only throws an interesting light on their origin, but at the same time furnishes a time clock to determine geological age, which has already proved invaluable.

Following a brief introduction to the subject of radioactivity the author discusses the distribution of radioactive material in the earth. After a general presentation of the radioactive heat sources, the theories of Jeffreys, Joly and Holmes with reference to the rate and mode of cooling of the earth and its geological consequences are discussed at length, especially Joly's theory of magmatic cycles.

The "lead method" of age determination by means of the lead:uranium and lead: thorium ratios are exhaustively reviewed as well as the radioactive constants involved in the age calculations. The helium method and the pleochoric haloes are rightly given a secondary place as age indicators, which detracts nothing from their own interest nor from the importance of the phenomena which they represent.

The monograph presents a thorough review of the aforementioned subjects, tempered by a sound and impartial judgment of a field to which the author has himself made most valuable contributions.

S. C. LIND

Introduction to Theoretical Physics. LEIGH PAGE. Pp. 587+x, 201 figs. D. Van Nostrand Company, 1929. Price $6.50.

This book is a noteworthy contribution to American literature in physics. It fills adequately the lamentable hiatus which has existed between our text books in general college physics and advanced treatises on more specialized subjects. Those of us who for years have attempted by courses of lectures to bridge over this gap in a systematic, unified way welcome this book as the first adequate text book of its kind which has been written for the American student.

The subject matter is divided into five main divisions, dynamics, hydrodynamics, thermodynamics and the kinetic theory of gases, electromagnetism and optics and spectroscopy. The introduction (39 pages) presents the elements of the vector analysis which is systematically used throughout the book in the mathematical formulation of the subject matter. The only mathematics required of the reader in advance is a good working knowledge of the differential and integral calculus and an acquaintance with the elements of differential equations.

The book is profusely illustrated and numerous problems have been interspersed through the text.

The style is lucid and the treatment in the main logical and clean-cut. In the section on mechanics one might quarrel with the casual introduction of mass, without definition or dis-

cussion of its significance, but in this the author has at least the preponderance of precedent in his favor.

The printing and binding are attractive and serviceable.

JOHN T. TATE

Probleme der Modernen Physik. Edited by P. DEBYE. Pp. 221+viii, 52 figs. Verlag von S. Hirzel, Leipzig, 1929. Price RM 18.00.

However productive the scholarship of a scientist who is at the same time a great teacher it is doubtful whether it can ever measure up in importance to the impress which he makes on the lives and thoughts of the hundreds of students with whom, in the course of a life time, he has come in contact. Arnold Sommerfeld is a great productive scholar but this collection of monographs, written by his former students and dedicated to him on his sixtieth birthday is a monument to his greatness as a teacher.

The book is a collection of twenty-eight wholly unrelated articles published in the order in which they were received. They deal with almost every phase of modern physics and no review of them is possible. The authors who contributed are: O. Blumenthal, Aachen; S. Bochner, München; E. Buchwald, Danzig-Langfuhr; P. Debye, Leipzig; P. P. Ewald, Stuttgart; E. Fues, Stuttgart; R. Glitscher, Wilhelmshaven; H. G. Grimm, Würzburg; W. Heisenberg, Leipzig; K. F. Herzfeld, Baltimore; D. Hondros, Athens; L. Hopf, Aachen; W. Kossel, Kiel; A. Kratzer, Münster; J. Kunz, Illinois; A. Landé, Tübingen; A. Laporte, München; W. Lenz, Hamburg; F. London, Berlin; F. Noether, Breslau; H. Ott, München; W. Pauli jr., Zürich; L. Pauling, Pasadena; W. Rogowski, Aachen; A. Rubinowicz, Lemberg; R. Seeliger, Greifswald; H. Seyfarth, München; A. Unsöld, München; Gr. Wentzel, Zürich; H. Wolff, Würzburg.

JOHN T. TATE

International Critical Tables, Vols. III and IV. Published for the NATIONAL RESEARCH COUNCIL. McGraw-Hill Book Company, Inc., New York, 1928.

Volumes III and IV of this monumental work contain material of interest primarily to the physical chemist. Volume III, prepared with the assistance of 62 cooperating experts, 20 of whom are foreign, presents data on pressure-volume-temperature relations for one phase systems (density, specific gravity, thermal expansion, compressibility) and phase-equilibrium data (vapor pressure, boiling point, critical-point constants, solubilites, vapor pressure lowering, boiling point elevation, P-T-X relations) for systems containing the vapor state. Volume IV, prepared with the assistance of 37 experts, 21 of whom are foreign extends the data on phase equilibrium to systems without the vapor phase (triple points, transition points, melting points, freezing-point-solubility data, cryoscopic data, effect of pressure). In addition there are tables of osmotic pressures and of surface properties (surfaces tension, surface energy and related properties, including the properties of thin layers and of surface solutions).

JOHN T. TATE

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE NEW YORK MEETING, FEBRUARY 22–23, 1929, JOINT MEETING WITH THE OPTICAL SOCIETY OF AMERICA

The 156th regular meeting of the American Physical Society was held in New York City on Friday and Saturday, February 22 and 23, 1929, as a joint meeting with the Optical Society of America. All sessions were held at Columbia University.

The Optical Society held regular sessions for the reading of papers on Friday morning and afternoon and on Saturday morning.

On Friday afternoon the two Societies had a joint session at which time Professor R. A. Millikan of the California Institute of Technology delivered an address on "*Cosmic Rays.*" The two Societies met again in joint session on Saturday morning and listened to an invited paper by Professor H. B. Williams of the College of Physicians and Surgeons, Columbia University, on "*Some Physical Problems in the Field of Medicine.*"

The regular sessions of the Physical Society were held on Friday afternoon, Saturday morning and Saturday afternoon, the Saturday morning session being split into two sections. The presiding officers were Professor Henry G. Gale and Dr. W. F. G. Swann.

At the regular meeting of the Council of the Physical Society held on Friday, February 22, 1929, two were elected to fellowship, four were transferred from membership to fellowship and thirty-six were elected to membership. *Elected to Fellowship:* L. F. Curtiss, C. C. Kiess. *Transferred from Membership to Fellowship:* Arthur Bramley, Joseph W. Ellis, Joseph Kaplan, Vern O. Knudsen. *Elected to Membership:* R. Bowling Barnes, Henry A. Barrett, Paul W. Bennington, Sidney Bloomenthal, Carl T. Chase, Harold T. Clark, William E. Danforth Jr., George Z. Dimitroff, Walter B. Ellwood, Bruce E. Foster, Kenneth H. Goode, H. W. Herrington, H. L. Hull, J. McN. Hunter, Helen Johnston, Frederick L. Knowles, Victor K. La Mer, John Liska, Gordon L. Locher, Thomas C. MacKay, Warren A. Marrison, Edward D. McAlister, Wellington A. Parlin, Harry L. Parr, Harry G. Romig, Charles B. Sawyer, George L. Shye, Harlan E. Short, Philip T. Smith, Hertha Sponer, William J. Spring, Lars Thomassen, Wilmer H. Tucker, John E. Volkmann, William West, Clarke Williams.

The titles and abstracts of papers presented before the Optical Society of America will be found in the Proceedings of that Society, published in the Journal of the Optical Society of America and Review of Scientific Instruments.

The Abstracts of the thirty-eight papers presented before the American Physical Society are given in the following pages. Numbers 21, 24, 25, 26, 27, 35, 36, 37, 38 were read by title. AN AUTHOR INDEX will be found at the end.

W. L. SEVERINGHAUS, *Secretary*

ABSTRACTS

1. The positive column of the mercury arc. T. J. KILLIAN, Princeton University.—The mechanism of the uniform positive column of a mercury arc has been studied by means of the Langmuir probe electrode method. Measurements of the random electron and positive ion currents, electron temperatures and space potentials were made both along a diameter and along the axis of a long cylindrical tube. The mean free path of electrons in mercury vapor as given by the Langevin mobility equation ($\mu = 0.815e\lambda/mv$) was found to be somewhat smaller than that previously obtained by other methods. The ratio of the densities of electrons at any two points along a diameter is related to the difference between the potentials at the points by the Boltzmann equation, $n/n' = e^{eV/kT}$ where T is the temperature of the electrons. From 15 to 50 percent of the energy input per unit length, depending upon the electron temperature, is delivered to the walls by the recombination of positive ions and electrons.

2. Angular distribution of secondary electrons in helium. G. P. HARNWELL, Princeton University.—A beam of electrons was projected through a region of high gas pressure and the electrons emerging at various angles with the original beam were analysed. Three types of electrons were found: those which had been scattered with no loss of energy, those which had lost the exciting or ionizing energy, and also a group of very slow electrons with energies varying from 0 to 10 or 15 volts. One of these last two groups may represent the primary and the other the secondary electrons. The angular variations of these groups at large angles were very similar. At small angles, however, there were many more of the electrons with smaller energy. A possible interpretation is that this group represents the primary electrons and they predominate over the secondary electrons at small angles because they have retained a component of momentum in the forward direction. However, this evidence is not conclusive, and the behavior is not identical in other gases. But if this is the correct explanation it means that the primary electron gives up nearly all its energy to the helium atom and the excess over the ionization energy is carried away by the secondary electron.

3. The electrical breakdown of liquids. J. W. BEAMS, University of Virginia.—The time lag of the spark discharge through liquids as well as the spectrum emitted at the beginning of the spark have been studied by a method previously described (Journal Franklin Inst. 206, 809, 1928). The time lag decreases with increasing field strength. In some dielectrics such as kerosene oil, nujol or carbontetrachloride an impressed field of over 3×10^6 volts per cm is required to reduce the time lag to values less than 1.5×10^{-8} sec. also the fluctuations in the time lag are less than those observed for air and decrease with increasing field strength. When once a spark has occurred through a dielectric the time lag is decreased. The spectra first emitted in a discharge through a pure liquid appear practically continuous throughout the visible region in all cases investigated. In the spark between Mg electrodes 2mm apart in running water the spectrum first appearing is continuous followed by the Mg spark line at 4481A. and the Mg arc triplet 5184, 72, 67A which appear as emission lines. The arc triplet however appears as very faint absorption lines when the total light from the spark is observed.

4. Conditions for initiation of electrodeless discharges in gases. N. T. GORDON AND S. DUSHMAN, General Electric Co.—Experiments have been carried out to determine the minimum current through a copper coil which will suffice to start a glow in a bulb placed inside the coil when the latter is supplied with high frequency current from a vacuum tube oscillator. Neon, helium and oxygen have been investigated at pressures ranging from 0.1 mm to 40 mm and at the frequencies 8.26×10^5 (363 meters), 16.04×10^5 (187 meters) and 31.58×10^5 (95 meters).

For each frequency there exists a critical pressure at which the current through the coil required to initiate the glow is a mimimum. The following table gives the values observed for a bulb 7.6 cm diameter placed in a copper coil 12.7 cm in diameter and consisting of 23 turns.

Minimum Current and Pressure

Gas	363 meters	187 meters	95 meters
Neon	1.1 amp. (7.0 mm)	0.42 amp. (4.0 mm)	0.44 amp. (3 mm)
Helium	1.3 " (3.0 ")	0.49 " (1.5 ")	
Oxygen	4.8 " (0.3 ")	1.7 " (0.4 ")	0.65 " (0.2 mm)

The effect of varying the bulb diameter was investigated; also the influence of electrostatic fields (as distinguished from those of electromagnetic nature). The phenomena exhibit a parallellism with positive column discharges which would necessitate taking into account charges on the walls.

5. Ion paths in constant electric and magnetic fields. LEIGH PAGE, Yale University.—J. J. Thompson has shown that an ion with zero initial velocity describes a common cycloid in crossed fields and drifts at right angles to the plane of the fields with a velocity of cE/H. Gunn has shown that the mean drift velocity is independent of the initial velocity and Maris and Hulburt have found a similar drift in a gravitational field, but these authors have not investigated the ion paths in detail. By a simple transformation to a moving set of axes it is shown that the effect of a constant electrical or gravitational force **F** on ions passing through a constant magnetic field **H** is (1) to change the radius of the circular or helical path of an ion about the lines of magnetic force from $(mc)v_0/(eH)$ to $(mc/eH)(v_0^2-2uv_0\cos\theta+u^2)^{1/2}$ where v_0 represents the component of the initial velocity perpendicular to **H** and u is defined below, and (2) to cause the circular or helical path to advance with the constant velocity $u=(c\mathbf{F}\times\mathbf{H})/(eH^2)$ in a direction at right angles to both **F** and **H**. The paths are therefore curtate, common or prolate cycloids described by the same rolling circle.

6. Dependence of electron emission from metals upon field strengths and temperature. R. A. MILLIKAN AND C. C. LAURITSEN, California Institute of Technology.—This paper contains a full presentation of the reasons for believing, contrary to results recently obtained elsewhere, that field currents are only independent of temperature up to about 1100°K, and that at that temperature the energy of thermal agitation begins to assist the fields in causing the escape of electrons from metals. The precise form of function describing this dependence is not accurately determinable experimentally, but the form originally suggested by us fits the facts of observation thus far known satisfactorily, not better, however, than does the theoretical form suggested by Houston.

7. The caesium-magnesium photo-cell. V. ZWORYKIN AND E. D. WILSON, Westinghouse Electric and Manufacturing Co.—The values of the work functions of the alkali metals and their color-sensitivity curves indicate definitely that caesium is the most favorable material for use in photo-cells. The practical difficulties of handling caesium metal have been overcome in the caesium-magnesium cell, in which a freshly evaporated coating of magnesium not only binds an invisible layer of caesium to the walls of the cell, but also provides an electrical connection with the cathode terminal. Average color-sensitivity curves are given for more than twenty cells. They show that the maximum sensitivity lies at about 4850A, as compared with 4400A for pure potassium, 5390A for pure caesium, and 5560A for the human eye. The photoelectric properties of the cell are detailed by means of response-voltage curves, response-illumination curves and illumination limit curves. The maximum response for vacuum type cells is about 2 microamperes per lumen, and for gas-filled cells about 25 microamperes per lumen under normal operating conditions. Several commercial applications are described. Further development work is now in progress.

8. Non-linearity of photoelectric response near long wave-length limit. W. B. NOTTINGHAM, Bartol Research Foundation.—The fact that the long wave-length limit for thin alkali metal films coincides with the first line of the principal series was reported by Ives and Oplin

(Abstract 19, New York Meeting, Dec. 27, 1928). This observation naturally suggests that the photoelectric current produced by illumination of a wave-length very near this long limit might come about as a result of cumulative action of two light quanta, one producing a state of excitation and the second producing ionization. A test of this theory has been carried out with a cell having a cylindrical nickel anode and a concentric platinum cathode on which some potassium was distilled and later partly evaporated off. The above mentioned observation of Ives and Oplin was verified and the predicted non-linearity of the photoelectric current was found to exist. The current increased almost exactly nine fold when the light intensity was increased by a factor of three, thus showing that under this very special condition the photoelectric effect is the result of the cumulative action of two light quanta for each electron.

9. Determination of frequency and decrement by means of plate current variations of thermionic oscillator tubes. J. TYKOCINSKI-TYKOCINER AND R. W. ARMSTRONG, University of Illinois.—The intensity of the plate current feeding a thermionic oscillator varies with the frequency ω of a coupled circuit. If the condenser setting of the latter is varied and ω plotted against ΔI_p, resonance curves are obtained representing $\Delta I_p = f(\omega)$. These curves were investigated within a range of 150 to 100000 kc. The influence of filament current I_f, plate potential E_p, coupling k and damping decrement δ was studied. The existence of critical values I_f' and E_p' was discovered for which $\Delta I_p = 0$. Above these values $I_p = f(\omega)$ is represented by peaked resonance curves, below these values the curves are inverted showing a depression. The character and the maximum values of the $\pm \Delta I_p$ curves depend also on the coupling and damping coefficients of the circuits. With the exception of a narrow zone near the critical points, the ΔI_p curves were found to correspond to Bjerknes resonance curves obtained with a thermogalvanometer inserted in the coupled circuit. By compensating the steady part of I_p a sensitive method was developed for measuring the frequency and logarithmic decrement of oscillating circuits, parallel wire systems and antennae. No thermocouple or any other device need be inserted in the measured circuit. The constants of the latter remain therefore unaffected by measurements.

10. Measurement of amplitude ratio and phase difference at the ears due to a source of pure tone. F. A. FIRESTONE AND D. L. RICH, University of Michigan.—A life sized, man shaped dummy with a wax head was fitted with Baldwin receivers in its ears, having their diaphragms where the ear drum would normally be. The source of sound was a loud speaker unit connected to a pipe which had its opening flush with the roof of the building. The dummy was mounted horizontally above the source and was so arranged that it could be turned about its axis and also adjusted to different distances from the source. The voltages generated by the microphones in the ears were measured in magnitude and phase by a null method involving an alternating current potentiometer driven from the same oscillator that supplied the source. Harmonics were eliminated. Readings were taken with the source at varying azimuths around the head; at 256, 1024, and 1944 cycles per second; and at distances of 20, 50, 100, and 400 cm from the head. The measurements for the two lower frequencies agree within 15 percent and 15° with the values published by Hartley and Fry computed on the assumption that the head is a rigid sphere in free space. The measured and computed values at 1944 cycles do not agree so well.

11. Measurement of sound absorption coeffcients. PAUL E. SABINE, Riverbank Laboratories.—The time t_1 required for the reverberant sound from a source of acoustic power E_1 (ergs/sec) to decrease to the threshold i(ergs/cu. m) in a room whose volume is V cu. m and absorbing power is a square meters of complete absorption is given by the equation (1) $t_1 = (9.2V/av) \cdot \log_{10}(4E_1/av_1)$. With a source whose acoustic output can be varied in known ratios a is found by the equation (2), $a = 9.2V/v) \log_{10}(E_1/E_2)/(t_1 - t_2)$. Using a telephonic loud speaker a linear relation between the logarithm of the current input and the reverberation was found, but the slope of the line, assuming E proportional to the square of the current was greater than a similar straight line using a number of simultaneously speaking organ pipes as the variable source. Measurements based on equation 2, using a loud speaker source gave higher values of the absorption coefficients than those based on equation (1) using

the same source. Intense tones gave higher coefficients than faint tones of same pitch and quality, as did also complex tones compared to pure tones of same pitch and intensity. Experiments indicate that the absorption coefficient of a porous material is a function of pitch, quality, and intensity so that reverberation measurements should be made under specified conditions as to these three factors.

12. Repeated reflection of atoms from crystals. A. ELLETT AND H. A. ZAHL, State University of Iowa.—The beam of cadmium atoms specularly reflected from a halite crystal impinging upon a second crystal is specularly reflected only when incident upon this crystal at the same or nearly the same angle at which reflection from the first crystal took place. When both angles of incidence are the same the entire beam incident upon the second crystal appears to be specularly reflected. A change of ten degrees in the angle of incidence upon the second crystal causes a marked loss of intensity in the specularly reflected beam, and it disappears when the angles differ by 25° to 30°. Under the latter conditions the beam specularly reflected from the first crystal is scattered at random by the second giving rise to a typical cosine distribution. These results show that the probability of specular reflection depends in a critical manner upon the velocity of the incident atoms. The probability of reflection of atoms whose velocity differs from the critical velocity by ± 15 meters per second is evidently less than half the probability at the critical velocity, and we may conclude that the "resolving power" is between the limits 0.01 and 0.05.

13. Intensities of general x-radiation proceeding from an atom in different directions. WILLIAM DUANE AND J. C. HUDSON, Harvard University.—Experiments have been described (William Duane, Proc. Nat. Acad. Sci., 14, 450, (1928)) which showed that, when a homogeneous stream of electrons impinges on mercury vapor atoms, a considerable amount of radiation proceeds forward in the direction of motion of the electron stream, as well as at right angles to that direction. The radiation projected forward was several times as intense as that projected at right angles. As mentioned before, this might have been due to the fact that the former came from a thicker layer of mercury vapor than did the latter. The object of the experiments described in this paper has been to investigate the intensities of the radiation projected (a) at 45° from the direction of motion of the electrons and (b) exactly opposite to this, at 135°. These two beams must have come from the same thickness of mercury vapor. The intensities of the beams were measured both by the ionization method and by photometering the photographs shown at this meeting. It appeared that the radiation projected forward at an angle of 45° from the direction of motion of electrons was about twice as intense as that projected backward at an angle of 135° from the same direction.

14. Determination of the orientation of metallic single crystal specimens by high voltage x-rays. THOMAS A. WILSON, General Electric Company, and Dept. of Chemistry, Union College.—The specimens involved in this work were single crystals of silicon steel which had been grown in strip form. For various reasons, the orientations of these specimens had to be determined by the Laue method. The usual 30 kv radiation from a Mo target was unsuitable for this work because of its low penetration. The source of radiation used was a Coolidge deep-therapy tube, with tungsten target, which was operated at 270 kv peak. The crystal under examination was mounted in a goniometer so that patterns could be obtained with the crystal in various positions with respect to the x-ray beam. When a photograph showing some easily recognizable symmetry was obtained (2-fold symmetry was sufficient) the orientation of the crystal was derived by use of the gnomonic projection. The method is adapted for quantity determinations because of its speed.

15. The relation between the continuous and line spectra of x-rays from thin targets. D. L. WEBSTER AND W. W. HANSEN, Stanford University.—The process of K-electron ionization by cathode-ray impact has a continuous-spectrum counterpart in the emission of a quantum of any frequency above the K limit. The ratio Q, of the probability of the former process to that of the latter, appears for thick targets of silver to be constant within reasonable limits of error. (Proc. Nat. Acad. Sci., June, 1928). The inference that it is likewise constant

for thin targets is subject to much wider limits of error. However, estimating the form and intensity of the thin-target continuous spectrum of silver by slight modification of Kulenkampff's data for aluminum (Ann. d. Physik., Nov. 1928), the probability of the above continuous-spectrum process can be calculated. It is found approximately proportional to measured Kα-line intensities between 25 and 85 kv (Proc. Nat. Acad. Sci., Sept. 1928). This furnishes additional evidence that Q is constant even for thin targets. A formula for either of these probabilities, suggested by simplification of the above calculations, is constant $\times U^{-n} \log U$, where $U = V/V_K$. With $n = 0.65$, obtained from Kulenkampff's data, this formula gives the line intensities within about 5 or 10 percent; with $n = 0.75$ or 0.80, it holds within 2 percent.

16. A high potential electrostatic voltmeter. S. W. BARNES AND F. K. RICHTMYER, Cornell University.—This electrostatic voltmeter departs from the common two-sphere-and-dumb-bell type in having but two spheres between which the electrostatic forces act. The feature of the instrument is the arrangment for getting rotational movement from the vertical displacement of the upper sphere. This sphere is supported by a coiled spring and two fibers which are caused to wind in opposite directions around a small cylinder on the sphere by the twist of the spring. The fall and rotation of the suspended sphere is proportional to the square of the difference of potential of the spheres. The advantages of this type are those of relative small size and flexibility. The range of the instrument may be changed by varying the distance between the spheres. One designed to read to two hundred kilovolts has detected one hundred and ten volts when the scale was reduced by raising the lower ball. Ageing the coiled spring prevents zero drift.

17. Compressibility of crystals and atomic fields. N. RASHEVSKY.—Westinghouse Electric and Mfg. Co.—A system of submicroscopic cracks is usually made responsible for the great difference between the actually found tensile strength of crystals and the theoretically computed one. It is pointed out that this system of cracks should have also an effect on the compressibility. It is shown that the compressibility of an ideal crystal may be considerably smaller than that of a real crystal. Since the compressibilities of crystals are used to calculate the exponent of the force of repulsion between ions (resp. atoms), the effect of the cracks will be to give us too low values for this exponent. Possible ways of investigating this influence are suggested.

18. Atomic order in ferromagnetism. L. W. MCKEEHAN, Yale University and O. E. BUCKLEY, Bell Telephone Laboratories.—The fields surrounding a paramagnetic atom in a ferromagnetic substance cannot possess spherical symmetry, even in a cubic crystal. The magnetic field has at least one distinguishable axis determined by the resultant magnetic moment of the atom. The mechanical field, responsible for cohesion and rigidity, must also have distinguishable lines or planes, and these must be definitely oriented with respect to the magnetic axis (but differently in atoms of different elements) to account for magnetostriction. The degree to which such distinguishable parts of different atoms in a specimen have a common orientation may conveniently be called its degree of magnetic order or mechanical order. In alloys the two sorts of atomic order may be inconsistent. The effects of mechanical, chemical and thermal processes upon mechanical order are predictable and the profound changes in magnetic behavior under weak and moderate magnetic forces which can thus be produced are thereby more easily explained. It becomes possible to write specifications for a ferromagnetic material with desired combinations of properties. Measurements of electrical resistance disclose the existence of atomic order in cases where magnetic and mechanical measurements are incompetent. Mechanical order may be of importance in some of the diamagnetic metals.

19. The Barkhausen effect in iron nickel and permalloy. RICHARD M. BOZORTH, Bell Telephone Laboratories, Inc.—Experiments show that the changes in magnetization which take place suddenly in large groups of atoms (Barkhausen effect) account for the whole change in magnetization over a considerable part of the hysteresis loop. Substantially all of the groups which act as magnetic units on the steeper parts of the loop are large enough to be detected

with a search coil and amplifier. The apparent large differences in the effect in various materials, and in the same material in different forms, are due to the different rates of decay of eddy-currents in them. The average size of the group is of the order of 10^{-7} cm³ for the steeper parts of the hysteresis loops for annealed iron, nickel and permalloy, for hard worked iron, and for a single crystal of iron.

20. Capillary phenomena in non-circular capillaries. W. O. SMITH AND PAUL D. FOOTE, Mellon Institute of Industrial Research.—The height of rise of a liquid of density ρ and surface tension σ in a cylindrical capillary of any section is shown to be given by $h=(\sigma P \cos\theta)/\rho g A$ where P is the perimeter of the tube, A its area of section, θ the angle of contact and g the acceleration of gravity. Application is made to square and elliptical tubes. Data are given for the rise of carbon tetrachloride and water in elliptical capillaries of various eccentricities. The above formula gives much better agreement than the one commonly used viz. that for a circular tube with radius equal to the geometric or arithmetic mean of the semi-axes.

The vapor pressure over the meniscus is shown to be given by $p-p_0=(d\sigma P \cos\theta)/(\rho A)$. A more accurate formula is $\log p_0/p=(d_0\sigma P \cos\theta)/(\rho-d)(p_0 A)$; p_0 is the vapor pressure over the free liquid, p that over the meniscus, and d_0 the vapor density over the free liquid.

21. A new system of dynamics. ARTHUR E. RUARK, Mellon Institute, Gulf Oil Companies and University of Pittsburgh.—The differential character of the equations of motion implies that a dynamical system is governed by laws operating with a precision beyond the limits of detection by experiment. This feature is undesirable, and it seems logical to introduce the general principle that *all physical phenomena can be described without the use of infinitesimals or infinites.* Like many other common sense physical postulates, this leads to surprising consequences. It requires us to use calculus of finite differences in formulating basic physical laws. In dynamics, the use of this calculus yields terms corresponding to the fact that *the configuration is known only when we observe it and must be arbitrary at intermediate times.* Example: If a "uniformly moving particle" is observed every second we find experimentally that $\Delta^2 x/\Delta t^2=0$, which replaces Newton's law. Integrating, $x=Ft+G$, where $F=\Sigma F_n \sin 2\pi nt$ and G is a similar arbitrary Fourier series. Relativistic dynamics may be attacked through a finite variation principle, replacing the geodesic law, and is not yet satisfactorily worked out. For small systems, finite dynamics should be connected with the indetermination principles of Heisenberg (Zeits. Phys. **43**, 172) and of the author (Proc. Nat. Acad. **14**, 322). The philosophic advantages of this formulation are obvious.

22. Application of the Fermi-Dirac statistics to specific heats of solids. A. T. WATERMAN, Yale University.—It is assumed that a solid consists of a system of harmonic atomic oscillators, each with three degrees of freedom. On applying the Fermi-Dirac statistics to such an assembly the mean energy per oscillator is found to be $U=3kTG(A)/F(A)$, where $F(A)$ and $G(A)$ are the Fermi integrals. For the classical state of the assembly $U=3kT$, and the specific heat $C_v=3Nk$, in agreement with the Dulong-Petit law. In the limiting case of extreme degeneracy C_v is proportional to the absolute temperature, vanishing at 0°K. The computed form of the specific heat curve over the intermediate range is roughly that found experimentally, but shows no point of inflection. According to this view-point the departure of the atomic heat for a given element from the Dulong-Petit value is due to increasing degeneracy in its system of oscillators. On arranging the elements in order of increasing degeneracy at a given temperature this order is precisely that of the observed departure from the Dulong-Petit law. The temperatures however at which marked departure from the Dulong-Petit specific heat value occurs on this hypothesis are in every case of the wrong order of magnitude, being too low.

23. Essay toward a new logic in physics. JOHN Q. STEWART, Princeton University.—Types of physical atomicity are molecules, electrons, and photons. Corresponding field theories are: heat and hydrodynamics, electromagnetic theory, and wave theory of light. In the microscopic theories three symmetrical equations express the energy of the "degree of freedom" as $\frac{1}{2}kT$, eV, $h\nu$, respectively. Thus temperature, electrostatic potential, and frequency are in a sense the same sort of thing. Likewise Boltzmann's constant, k, "Millikan's constant," e, and

Planck's constant, h, are symmetrically related. As k has dimensions of entropy, the suggestion is that entropy occurs in three modes, being analogous with charge and action. On this view the distinction should carefully be maintained between mechanical work, and energy increments which are associated with variations in intropy, charge, or action. The argument that entropy is explained by probability can be inverted, probability being defined by reference to a prior intuition which corresponds to the second law of thermodynamics. Although reasoning by broad analogy is received with caution, it is certain that thermodynamics offers an advanced base for exploring toward a synthesis of physical laws. For such an attempt guidance is found in Leibniz rather than in Newton.

24. Further combinations in the spark spectrum of nickel. R. J. LANG, University of Alberta.—The lowest term of the first spark spectrum of nickel is a doublet D term from the configuration d^9. The value of these terms relative to $(d^8s)^4F'$ was reported in a previous paper to be -6884 and -8391 cm^{-1}. These term values were derived from combinations between this lowest D term and the following terms of the d^8p configuration: $^4D'$, F, G'; $^2D'$, F, G'. The remaining twelve terms of the d^8p configuration namely: $^4S'$, P, D'; $^2S'$, P, D'; ^2P, D', F; ^2F, G', H; have now been found to combine with the lowest ^2D term resulting in twenty-six ines lying between 1537 and 1250A.

25. The spectrum of the aurora borealis. JOSEPH KAPLAN, University of California at Los Angeles.—The difference $^1D_2-{}^3P$ in the O I spectrum can be calculated by assuming that the ratio of the differences $^1D_2-{}^3P$ and $^1S_0-{}^1D_2$ in O I is equal to the same ratio in O III. The value obtained is 1.96 volts. Bowen, by entirely different considerations obtained a value equal to 2.05 volts. The 1.96 value for the difference $^1D_2-{}^3P$ and the 2.23 value for the difference $^1S_0-{}^1D_2$ have been used by the author to explain the excitation of the α bands 6470, 6323 and 5925 which are the only α bands that have been observed in the aurora. These bands are excited by collisions between metastable oxygen atoms in the $^1S_0$ and $^1D_2$ levels and metastable nitrogen molecules in the A_3 level. The presence of N_2 in this level can be explained by considerations similar to those that enter into the explanation of the nitrogen afterglow. This method indicates also that there are very few metastable nitrogen atoms in the aurora. The level B_{10} (the initial level of 6323) can also be excited by collisions between N_2 in the A_0 state and N_2^+ in the upper level of the two most intense bands in the aurora. The energy available agrees exactly with that necessary for the transition $A_0 \rightarrow B_{10}$.

26. Active nitrogen. JOSEPH KAPLAN, University of California at Los Angeles.—Recently Cario and the author have called attention to evidence for the existence of metastable atoms and molecules in the nitrogen afterglow. The new value of the heat of dissociation of nitrogen to which attention has been called independently by Birge, Mulliken, Herzberg and the author, makes two reactions in the afterglow especially interesting. The heat of dissociation of nitrogen proposed by Herzberg and the author is equal to 9.1 volts. Therefore, by recombination between a normal nitrogen atom and one in the metastable ^2D state, it is possible to excite the B_{11} level of the molecule, since the energy available in this process is 11.47 volts and the energy necessary for the excitation of the B_{11} level is 11.46 volts. Instead of a recombination between a normal atom and a metastable one we can consider the recombination between two normal atoms to form a metastable molecule possessing 9.1 volts and then the subsequent excitation of this by an atom in the ^2D state, once more giving a molecule in the B_{11} level. In this way we can account for the fact that the bands arising on the B_{11} level are the most intense ones in the afterglow.

27. The continuous spectrum of hydrogen. JOSEPH KAPLAN, University of California at Los Angeles.—The recent experiments of Jones and Whiddington have shown that the excitation potential of hydrogen at 12.6 volts is the most probable one at low voltages. They have failed to observe the excitation of the triplet levels. Because of this the explanation of the continuous spectrum of the hydrogen molecule proposed by Winans and Stueckelberg is modified and most of the spectrum is now said to arise in transitions between the C level and the new 1^3S level of Heitler and London. This explanation is in good agreement with the failure

of Oldenberg to observe the continuous spectrum in argon-hydrogen mixtures and with the disappearance below 13.5 volts of the blue glow in the experiments of Horton and Davies. It also makes possible the explanation of the new observations of Jones and Whiddington of energy losses in electrons, corresponding to the entire range from about 8 or 9 volts to zero. These are said to correspond to transitions from the 1^1S level to the C level.

28. Dependence of ultra-violet reflection of Ag on plastic deformation. HENRY MARGENAU, Yale University.—The change in electrical conductivity of metals with mechanical strain suggests the possibility of a dependence of optical reflecting power on plastic deformation. To study this matter, and to obtain additional evidence with regard to the nature of cold working, the behavior of the minimum of reflecting power of silver in the near ultra-violet (at 3160A according to Rubens and Hagen) was examined for silver surfaces of varying degrees of strain, produced by vigorous and moderate polishing, etching, and electroplating. Reflection curves were obtained by measuring directly, by means of two quartz photoelectric cells, incident and reflected intensities. It is shown that the minimum is very low and lies at 3160A, in accordance with Ruben's and Hagen's measurements, only for highly polished plates. For unstrained surfaces it is shifted to lower wave lengths by about 20A and the reflecting power rises appreciably. The shift has also been verified photographically. It is interesting to note that the effects of cold working upon the minimum are in certain respects analogous to those produced by heating.

29. Ultra-violet fluorescence of IBr and I_2. F. W. LOOMIS AND A. J. ALLEN, New York University.—Using a quartz apparatus of special design, in which the fluorescence tube is completely surrounded by a water-cooled Hg arc, a fluorescence spectrum has been obtained from IBr at low pressures. It lies entirely in the ultra-violet, and is distinctly different from the spectrum of I_2 fluorescence in this region. (Oldenberg, Zeits. Phys. **18**, 1 (1923)). A series of close groups of lines is excited by λ1849, and the strongest line in each is represented by $\nu = 54{,}048 - 276.2p + 1.28p^2$, where p is an integer. At high values of p the even terms are too weak for identification, being lost in a complicated line structure, but the odd terms can be traced as strong, single lines as far as $p = 43$. Near λ2500 the line structure ceases, and a number of diffuse, headless bands extend to λ3700. This phenomenon is similar to that in I_2, where the transition to continuous bands takes place abruptly at λ2400. High dispersion photographs of the latter bands failed to reveal any line structure. The fluorescence series of I_2 excited by λ1849 and λ1942 have been photographed with resolution sufficient to show the rotational structure, permitting a correlation with the visible resonance series excited by λ5461. No fluorescence could be obtained with Br_2, ICl, or BrCl.

30. Resonance radiometry. A. H. PFUND, Johns Hopkins University.—So as to reduce the effect of spurious disturbances which limit the usefulness of usual radiometric apparatus, a system involving resonance has been constructed. A single-junction thermopile of low heat capacity is illuminated intermittently at regular intervals, and is connected to an underdamped galvanometer tuned to the period of intermittency. The deflections of this galvanometer are amplified. If a thermopile amplifier be used, the sensitivity of the best present-day radiometers is equaled. If, however, a photoelectric amplifier be employed, a thousand-fold increase is realized. By employing a tuned system throughout, great immunity from spurious disturbances is attained.

31. The effect of temperature on the absorption bands of fused quartz in the infra-red. W. A. PARLIN AND A. H. PFUND, Johns Hopkins University.—Specimens of fused quartz, ranging in thickness from 2.0 mm for the 3μ region, to $4 \cdot 10^{-4}$ mm for the 8μ region, were used. Measurements were taken at room temperature and at 850°C. When sufficient energy was available, an echelette grating was used for greater dispersion. In accord with previous work, the absorption band in the region of anomalous dispersion at 8.5μ was found to shift toward the red with increasing temperature. With higher resolution, fine structure bands were found which did not shift with temperature, but underwent marked changes in intensity. Several sharp bands between 2 and 4μ were found to remain fixed as the temperature was changed. A

broad band at 12.5μ also remained fixed as the temperature was changed. It was found that inside of the strong bands, the absorption was less at high temperatures, while outside the band, the reverse was the case.

32. Infra-red absorption of formaldehyde vapor, I. E. O. SALANT, National Research Fellow, and W. WEST, New York University.—Ultra-violet absorption bands of the vapor of formaldehyde, H_2CO, show rotational lines corresponding to a quite small moment of inertia of the molecule (Henri and Schou, Zeits. f. Physik., 49, 784 (1928)); consequently comparison of these bands with the infra-red rotation-vibration bands of formaldehyde offers an unique opportunity for the study of the theory of band spectra.

The measurements reported here, extending from the visible to 3.6μ, were made with a spectrometer having two sixty-degree quartz prisms, a Moll linear thermopile, thermo relay and Zernicke and Moll moving-coil galvanometers. The strongest bands, listed in the order of their intensities, were found at [3.31, 3.38, 3.47], 218, [1.77, 1.84], 191, [144, 1.40], 1.25μ. The 1.4 and 1.8μ bands appear as doublets, the 3.4μ band as a triplet with evidence of rotational structure. The separations of the lines in the 3.4μ band appear, however, markedly smaller than would be indicated by the moment of inertia derived from the ultra-violet lines. This work is being extended by means of an echelette grating spectrometer.

33. Effect of high frequency waves on the optical properties of water. A. BRAMLEY, Ph.D., Bartol Research Foundation of the Franklin Institute.—When a light of a given frequency ν is passed through a dielectric transparent to that frequency, which forms part of a parallel plate condenser, the light wave can be changed in character in two ways, when electromagnetic waves of frequency P are impressed on the condenser. First, the light train will be modulated (Abs. Dec. 1928) and secondly, the light, if it is initially plane polarized will become elliptically polarized due to the medium becoming double refracting. On measuring the amount of double refraction, i.e., the Kerr constant, for various frequencies of the oscillation applied to the Kerr cell, it was found to go through a series of maxima and minima of abnormally large amount compared to that for static electric fields. The change in frequency of the light wave produced by the action of the high frequency waves also showed the same kind of periodic phenomena with change of frequency; the frequency change of the light wave varied from 0 to 0.06A°. These results indicate that the medium, water, has a set of absorption bands for high frequency radio waves which change the action of the medium for light waves passing through it.

34. Photographic spectral energy measurement with a spiral aperture disc. BRIAN O'BRIEN, Buffalo Tuberculosis Association, Perrysburg, N. Y.—A disc with a profile cut to a logarithmic spiral is rotated before the slit of a spectrograph in such a manner that, if t = integrated time of illumination of any point on the slit, $\log t = h$, where h = height above a reference point of the slit. The illumination cycle is repeated 60 times per sec. Assuming the reciprocity law and that the plate integrates intermittant exposure, then the height of the spectrum, $h' = \log I$, where I = intensity and $h' = H - h$, where H = total slit height. With the arrangement used, error in h' due to failure of reciprocity law opposes the error due to failure of plate to fully integrate the intermittent exposure, providing light intensity at the plate is less than "optimal" intensity described by Kron (Eder's Jrbch. p. 6, 1914) and investigated by Jones and collaborators (J.O.S.A. 7, p. 1079, 1923, et. seq.). The magnitude of these two errors has been investigated for variations in h' from 0 to 2.00 over a range of intensities (1 to 10,000) for six photographic emulsions of widely different speed and color sensitivity, over the range λ6000A to λ2200A. The separate errors in h' (reciprocity and intermittency failure) range from 0.04 for a fast emulsion to 0.15 for a slow emulsion for an intensity range of only 1 to 20, but the compensation of the two is complete within 0.015 in every case investigated. An intensity scale is impressed directly on the spectrum image by a comb in front of the spectrograph slit. A reliable means of spectral energy measurement is thus provided, with systematic errors much less than variations in emulsion sensitivity over the surface of a plate.

35. Generalizations of Planck's formula. ARTHUR E. RUARK, Mellon Institute, Gulf Oil Companies and University of Pittsburgh.—In 1926, the writer studied the black-body radiation

laws which are obtained by assuming that the probabilities of absorption and emission are $B_\omega\rho+C_\omega\rho^2+\cdots$ and $A+B_\omega\rho+C_\omega\rho^2+\cdots$, respectively, instead of $B_\omega\rho$ and $A+B_\omega\rho$, used by Einstein. By studying the data of Rubens and Michel it was concluded that over their wave-length range, and up to about 3000°C, there is no convincing evidence of systematic deviations from Planck's formula of the kind required by these assumptions. Strum (Zeits. Phys. **51**, 287) has published a radiation law based on the inclusion of terms in ρ^2 in the probabilities. The writer found, however, that (on the old mechanics) the average energy of Brownian movement, $3kT/2$, is not obtained by using such a law. The interchanges of momentum between atom and radiation were calculated on the basis adopted by Einstein,—namely, quanta which merely induce transitions pass over the atom without change in frequency or direction. The effect of modifying this assumption, and of using the new mechanics, remains to be investigated. In conclusion, stellar spectra appear to offer the most favorable opportunity for discovering deviations from Planck's law, in case they exist.

36. On hysteresis in physico-chemical systems. N. RASHEVSKY, Westinghouse Electric and Manufacturing Co.—Understanding by hysteresis the fact that the state of a system is determined not only by the instantaneous values of parameters, which characterize the external conditions, but by the previous history of the system, it is shown that whenever the equations, which determine the equilibrium of the systems, have several solutions for the same values of the parameters, the system will exhibit hysteresis. It is shown furthermore, that under certain conditions the behavior of the system will depend not only on the previous state of external conditions, but also on the rate of change of the latters.

37. **The dielectric constant of air at various radio frequencies.** F. L. TALBOTT, Catholic University of America.—The dielectric constant of air was measured by a heterodyne method. A null system was used, the change in capacity due to the admission of air to the test condenser being compensated for by means of a standard precision condenser in series with it. A 65 plate aluminum condenser of about 2000$\mu\mu$f capacity was used for the test. The correction for capacity due to solid supports was calculated from the capacity of the condenser in vacuum and the capacity when it was immersed in an oil of known dielectric constant. Measurements were made at frequencies ranging from 28 to 1100 kilocycles, No change of the dielectric constant with frequency was found. The mean value obtained was 1.000547.

38. The development of "thermodynamic symbolism." JOHN Q. STEWART, Princeton University. Physical formulae possess *literal meanings*—correspondences, experimentally verifiable, with natural phenomena. They possess also *symbolic meanings*, in that concepts and relations which have been developed in a given field may exhibit a one-to-one correspondence with those in another field. This is illustrated by a study of a simple mechanical system which consists of a mass sliding on a rigid rod, the rod being fastened radially to a central rotatable shaft. The well-known "adiabatic invariance" of angular momentum is only one of a whole series of thermodynamic analogies here. The "working body" may acquire rotational energy ("heat") from other shafts rotating at various frequencies ("temperatures"). It may pass through a Carnot's cycle: every thermodynamic relation and concept finds its counterpart. In particular, frequency can be determined in a fundamental manner, independently of the idea of time. Again, an electrostatic condenser may be the working body, acquiring charge ("entropy") at different potentials ("temperatures"). Thus the indications are that the relations of thermodynamics may be capable of providing a *physical symbolic logic*. Its general statements will be translated to a given special field by a table of equivalent concepts. Further study is required.

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